PRINCIPLES OF
ORGANIC CHEMISTRY

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BY

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PREFACE

The present work originated in connexion with the author's teaching of organic chemistry to students reading for Pre-medical, First M.B., National Certificate, Pharmaceutical and General examinations in Chemistry. The theoretical section covers the syllabuses of the Higher School Certificate courses of the Universities of Oxford, Cambridge, and London, and of various professional bodies.

Students are apt to find organic chemistry difficult, although many of them can appreciate the logical sequence of certain main portions of the subject. The difficulty of mastering the first principles is increased by the introduction of complex compounds at an early stage, before their methods of preparation and characteristic properties have been described. An attempt has been made here to avoid such complexity in the earlier parts of the book.

The treatment does not claim to be exhaustive; the author has sought to curtail unnecessary material and to present the underlying principles as clearly as possible, in the hope of giving the student a sound foundation which will enable him to take full advantage of his further studies, whether in Chemistry, Biochemistry, Pharmacy, or Medicine.

References from larger works have been freely sought and important points embodied in the book.

The practical section, including tests, observations, estimations, &c., serves to supplement the theoretical section. In the concluding chapters, however, tests which

have no counterpart in the theoretical section have been added for students reading for pharmaceutical and medical examinations. The experimental data used to illustrate the calculation of results are taken from experiments by the author.

In conclusion the author desires to express his indebtedness to Dr. E. G. Cowley, Ph.D., M.Sc., A.I.C.; Mr. T. E. Green, M.A., B.Sc.; Mr. H. H. Hirst, M.Sc.; Mr. E. H. Ellis, B.Sc., and Mr. P. B. Fletcher, M.Sc., A.I.C., for reading the manuscript and offering valuable suggestions and criticisms; to Dr. E. C. Pickering, B.Sc., Ph.D., F.I.C., for reading the slip proofs; to Messrs. Courtaulds, Ltd., for information on cellophane manufacture; Messrs. Baird and Tatlock for permission to reproduce fig. 53; to the Institute of Chemistry for certain items of information, and finally to the Boards of Examiners and to the Controller of H.M. Stationery Office who have given him permission to reproduce questions from papers set by them and by the Civil Service Commissioners respectively.

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CHAPTER I

Molecular Formulæ and Molecular Weights

The word "organic" was originally applied to such substances as spirits of wine, sugar, fats, and other substances directly or indirectly concerned with animals or plants.

The composition of these natural products was first investigated by Lavoisier (1743–94). He showed that nearly all vegetable substances are composed of carbon, hydrogen and oxygen, whilst animal substances are composed of carbon, hydrogen and oxygen and in addition other elements, namely, nitrogen and sometimes phosphorus and sulphur.

The qualitative tests for elements in organic compounds are outlined later (p. 490).

It should be noted that:

1. The compounds containing carbon are far more numerous than the known compounds of any other element.

2. These compounds of carbon are related to one another, but differ widely in general behaviour from those of other elements, and consequently form a group by themselves.

3. The large number of the carbon compounds is due to the facts that:

(*a*) all the chief constituents of animals and plants are derivatives of carbon;

(*b*) the atoms of carbon have an extraordinary capability for combining with one another and with hydrogen to form compounds, and a great many compounds not known in nature have been prepared artificially in the laboratory.

4. Organic compounds, however, are limited to not more than four or five elements, e.g.:

(*a*) sugar, starch, tartaric acid, &c., consist of C, H, O;

(*b*) morphine, strychnine, &c., consist of C, H, O, N.

Formulæ

The formula of a substance can be easily deduced when the percentage composition of the compound is known.

Example.—A compound has the following percentage composition by weight:

Carbon, 40%; Hydrogen, 6·67%; Oxygen, 53·33%.

In order to deduce its formula:

1. Divide the percentage composition of each element by its atomic weight; the result gives the atomic ratio.

$$\text{Carbon,} \qquad \frac{40}{12} = 3\cdot33$$

$$\text{Hydrogen,} \qquad \frac{6\cdot67}{1} = 6\cdot67$$

$$\text{Oxygen,} \qquad \frac{53\cdot33}{16} = 3\cdot33$$

2. Divide the atomic ratios by their H.C.F., which in

this example is 3·33; the result gives the number of atoms of each element present, namely,

$$\text{Carbon,} \qquad \frac{3\cdot 33}{3\cdot 33} = 1$$

$$\text{Hydrogen,} \qquad \frac{6\cdot 67}{3\cdot 33} = 2$$

$$\text{Oxygen,} \qquad \frac{3\cdot 33}{3\cdot 33} = 1$$

The formula of this compound is therefore $C_1H_2O_1$ or CH_2O.

There are three substances which have the same percentage composition as the example just given; this frequently happens with organic substances. The three substances are:

Mol. Wt.

Formaldehyde of molecular formula $H \cdot CHO$, i.e. CH_2O. 30

Acetic acid of molecular formula CH_3COOH, i.e. $(CH_2O)_2$. 60

Lactic acid of molecular formula $CH_3CHOH \cdot COOH$, i.e. $(CH_2O)_3$. 90

The simplest formula, CH_2O, for all these compounds is known as the empirical formula, which may be defined as follows:

The Empirical Formula is the simplest expression of the ratio of the atoms.

Examples.—1. An organic substance has the following percentage composition by weight:

$$C = 66\cdot 7\%, \quad H = 11\cdot 1\%, \quad O = 22\cdot 2\%$$

Find its empirical formula.

2. Find the empirical formula of the organic substance which has the following percentage composition by weight:

$$C = 52 \cdot 2\%, \quad H = 4 \cdot 3\%, \quad O = 23 \cdot 2\%, \quad N = 20 \cdot 3\%$$

The Molecular Formula expresses not only the ratio but also the actual number of atoms in the molecule.

Methods for Determining Molecular Weight

In order to deduce the molecular formula of a compound it is necessary to determine its molecular weight. This can be done by

(A) Physical methods,
(B) Chemical methods.

(A) Physical Methods

These include:

1. Vapour density methods:

(a) Victor Meyer's method,
(b) Gay-Lussac's method,
(c) Dumas' method.

2. Depression of the freezing-point, or Cryoscopic method (sometimes known as Raoult's method).

3. Elevation of the boiling-point, or Ebullioscopic method.

4. Osmotic pressure method.

5. Lowering of vapour pressure (Menzies' method).

Note to Students.—The student should now turn to Chapter II, as the various methods for the determination of molecular weights outlined below should be studied separately and at leisure.

1. **Vapour Density Methods.**

These are based upon the hypothesis of Avogadro, which states that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. Hence the ratio of the weight of a given volume of any gas and the weight of the same volume of hydrogen under the same conditions gives the specific gravity (S.G.) or vapour density (V.D.) of the gas, that of hydrogen being taken as unity.

That is, $\text{V.D.} = \dfrac{\text{Molecular Weight of Gas}}{\text{Molecular Weight of Hydrogen}}$;

but   Molecular Weight of Hydrogen $= 2$,

i.e.   Mol. Wt. of Gas $=$ V.D. $\times$ 2.

Thus to find the molecular weight of a gas or of a volatile liquid or solid it is sufficient to determine its vapour density and to multiply this value by two.

Experimentally the vapour density is determined:

(*a*) by measuring the volume occupied by the vapour of a known weight of the substance at known temperature and pressure and reducing it to Standard Temperature and Pressure (S.T.P.); S.T. $= 0°$ C.; S.P. $= 760$ mm.

(*b*) by finding the weight of a known volume of the vapour of the substance at known temperature and pressure and reducing it to S.T.P.

(*a*) *Victor Meyer's Method.*

Victor Meyer's apparatus for determining the density of an unsaturated vapour consists of three parts:

1. A vaporizing tube A closed at B by means of an india-rubber stopper.

2. A heating jacket C which contains some constant-boiling liquid, e.g. water (b. pt. 100° C.); aniline (b. pt.

183° C.); xylene (b. pt. 140° C.); ethyl benzoate (b. pt. 213° C.). The boiling liquid is so chosen that its boiling-point is some 25° C. above that of the organic substance whose molecular weight is to be determined.

3. A graduated tube D filled with water, to collect the gas driven over during the experiment.

The apparatus is connected as in fig. 1. The liquid in the heater C is boiled, and the stopper B removed, while the air expands until a constant temperature is reached. A small glass stoppered bottle known as a Hofmann bottle, H, completely filled with a weighed quantity of the liquid or solid (about 0·05 gm.), is dropped into A, the bottom of which contains sand or asbestos to prevent breakage of the vaporizing tube. The stopper B is immediately replaced. The organic substance volatilizes and forces the stopper out of the bottle, and the expanding vapour drives over into the graduated tube D an amount of air corresponding to the volume it occupies. When equilibrium is reached the gas is corrected to S.T.P.

Let V be the volume at $t°$ C. and pressure p mm. of mercury, and V_0 the volume at S.T.P. Then

$$V_0 = V_t \times \frac{273}{273 + t} \times \frac{(p - w)}{760},$$

Fig. 1.—Victor Meyer's Vapour Density Apparatus.

where w is the tension of aqueous vapour at $t°$ C. (see table, p. 637).

Example.—An organic liquid has the empirical formula

$C_4H_{10}O$; 0·062 gm. of the liquid gave 23·2 c.c. of vapour at 50° C. and 720 mm. What is its molecular formula?

Calculation.—Volume at S.T.P. $= 23\cdot2 \times \dfrac{720}{760} \times \dfrac{273}{323}$

$$= 18\cdot57 \text{ c.c.}$$

18·57 c.c. of vapour weigh 0·062 gm.

18·57 c.c. of hydrogen weigh 0·00167 gm. (1 c.c. H_2 weighs 0·0000899 gm.).

$$\text{V.D.} = \frac{\text{Wt. of vapour}}{\text{Wt. of hydrogen}} = \frac{0\cdot062}{0\cdot00167} = 37\cdot1.$$

Mol. Weight $= 2 \times 37\cdot1 = 74\cdot2$;

∴ Mol. Formula is $C_4H_{10}O$;

Substance is C_4H_9OH, butyl alcohol, or
$C_2H_5OC_2H_5$, ethyl ether.

An improved form of Victor Meyer's apparatus (fig. 2) consists of a wide tube C which contains at the bottom a liquid of higher boiling-point than the substance of which the vapour density has to be measured. The substance is vaporized in the bulb A, and in doing so displaces its own volume of air, which is driven up the tube B, through a length of thick-walled indiarubber tubing attached to the side tube D, and into a graduated burette E. This burette is supported within a glass cylinder F, the bottom of the cylinder being closed either by being drawn down and connected with a stop-cock G, or by means of a cork pierced with a drainage tube and clip.

The liquid which is to be experimented upon is contained either in a small bottle with a glass stopper, or in a thin-walled glass bulb, which at the commencement of the experiment is hung from a wire M passing through the cork which closes the top of the tube B. The shape of this wire is shown on a larger scale at W. In the position shown the bottle hangs from the lower end of the wire, a loop of wire being attached to the neck of the bottle for the

purpose. On the wire being turned through two right angles by means of the handle M, the wire loop slips off the hook and the bottle falls down the tube B. A little asbestos or sand placed in the bulb A serves to prevent the bottle breaking the tube in its fall.

The volume of gas is read off in E when the water pressure has been adjusted by running off water through G until the pressure is the same inside the burette E as outside. The temperature is read by the thermometer T. The volume is then corrected to S.T.P.

It should be noted that:

(a) the boiling-point of liquid in the boiling tube should be at least 25° C. higher than the boiling-point of the substance;

(b) the vapour of the substance must not decompose.

Fig. 2.—Victor Meyer's Apparatus (improved form)

(b) Gay-Lussac's or Hofmann's Method.

A is a graduated tube about 85 cm. long and 35 mm. in diameter, filled with mercury and then inverted in a mercury reservoir R (fig. 3). It is surrounded by a jacket C through

which the vapour of a suitable liquid boiling at a known and constant temperature is passed. (Such liquids are mentioned above.) The liquid is boiled in a copper vessel D, and vapour escapes through the side tube E to a condenser (not shown in the diagram). As soon as the thermometer is at a constant temperature the reading is taken and a weighed quantity of the substance (0·05 gm.) contained in a small stoppered bottle is placed under the end of the barometer tube; it rises and is vaporized in the Torricellian vacuum. The level of the mercury is read before and after this, and the volume reduced to S.T.P.

The molecular weight is calculated as before.

The advantage of this method lies in the fact that vapour densities can be determined under greatly reduced pressures and therefore at temperatures far below the ordinary boiling-points of the substances; thus molecular weights of substances which under reduced pressures are not decomposed can be determined.

Fig. 3.—A. W. Hofmann's Vapour Density Apparatus

(c) *Dumas' Method.*

The apparatus consists of a globe-shaped vessel of capacity 200 c.c., the neck of which is drawn to a fine point

(fig. 4). This vessel is weighed and the temperature and pressure are noted. About 10 gm. of the liquid are introduced by warming the vessel and dipping it into the liquid and cooling. The globe is then immersed in an oil bath and heated at constant pressure to a temperature at least 25° C. above the boiling-point of the compound. The air is thus expelled by the vapour; as soon as the whole of the liquid has been vaporized, the point of the tube is sealed by means of a blow-pipe, and the temperature of the oil bath noted.

The globe is cooled, cleaned, dried, and weighed. The point is now broken under some water (or mercury), which rushes in and fills the globe completely; the latter is then weighed again and its volume is thus determined from the volume of water contained in it.

Fig. 4.—Dumas' Vapour Density Apparatus

Calculation.

Let W_1 be weight of globe + air; W_2, weight of globe + vapour.

$(W_2 - W_1) = W =$ Weight of vapour less weight of the volume (V) of air at $t°$ C. and pressure P mm.

Let V_0 be Volume of air at S.T.P.

Weight of Air $= V_0 \times 0.001293$ gm.,
    since 1 c.c. of air at S.T.P. weighs 0.001293 gm.

Weight of Vapour $= W + (V_0 \times 0.001293)$.

Weight of same volume of Hydrogen
$$= (V_0 \times 0.0000899) \text{ gm.}$$

$\therefore$ Vapour Density $= \dfrac{W + (V_0 \times 0.001293)}{V_0 \times 0.0000899}$.

2. Depression of the Freezing-point, Cryoscopic Method, or Raoult's Method (1883).

In order to understand this method for the determination of molecular weights it is necessary to remember certain obvious facts:

(*a*) Every pure liquid has a definite freezing-point, e.g. water, o° C.

(*b*) If a substance is dissolved in a liquid, the freezing-point of the solution is lower than that of the pure solvent, and for the same solvent and same solute the extent of the lowering is directly proportional to the concentration.

This is known as Blagden's Law.

(*c*) There are two types of compounds which dissolve in solvents, namely, electrolytes, such as mineral salts, and non-electrolytes, such as sugar and urea.

Electrolytes decompose into ions in solution, e.g.

$$Na_2SO_4 = 2Na^{\cdot} + SO''_4,$$

and are able to convey the electric current.

Non-electrolytes in the main neither decompose nor convey the electric current.

(*d*) In organic chemistry the cryoscopic method is used for non-electrolytes only.

Raoult in 1883 showed for non-electrolytes that most substances when dissolved in water or other solvents depress the freezing-point, and that this depression of the freezing-point is proportional to the number of molecules of the dissolved substance in a given weight of the solvent and independent of the nature of the substance. From this statement it is possible to deduce a formula for determining the molecular weight of a substance in solution.

Example.—It is found that when 1 part of sugar is dissolved in 100 parts of water it depresses the freezing-point 0·054° C., i.e. the solution freezes at −0·054° C. instead of at o° C.

If 10 parts of sugar are dissolved in 100 parts of water, the depression of the freezing-point is $10 \times 0.054° = 0.54°$ C., according to Raoult.

The molecular weight of cane sugar is 342, and if this weight expressed in grammes were dissolved in 100 gm. of water, the depression in the freezing-point would be $342 \times 0.054°$ C. $= 18.6°$ C. approximately.

Now it is found that when the molecular weights expressed in grammes of many such substances are dissolved in 100 gm. of water the depression of the freezing-point is $18.6°$ C. Such substances include

		Molecular weight
Cane sugar	.. ..	342
Urea ..	.. ..	60
Grape sugar	.. ..	180
Alcohol	.. ..	46
Resorcinol	.. ..	110

The figure 18.6 is constant for water and is known as the molecular depression of water, or the cryoscopic constant for 100 gm. of water.

Other solvents used in the cryoscopic method are

	Molecular depression (K)	Freezing-point (F.P.)
Acetic acid ..	39	$17°$ C.
Benzene ..	51.5	$5.5°$ C.
Phenol ..	72.7	$42°$ C.

The molecular depression of a solvent is a constant and is denoted by the symbol K. It is now possible to arrive at a definite formula for determining the molecular weight of a compound.

Let M be Molecular weight of substance,
K, Depression constant of solvent for 100 gm.,
w, Weight of substance taken,
d, Observed depression,
W, Weight of solvent taken.

If w gm. dissolved in W gm. of solvent give a depression d,

M gm. dissolved in W gm. of solvent give a depression

$$\frac{d}{w} \times M,$$

and since the depression is directly proportional to the concentration,

M gm. dissolved in 100 gm. of solvent give a depression

$$\frac{d}{w} \times M \times \frac{W}{100}, \; = \kappa$$

but this is equal to K. Hence

$$M = \frac{K}{d} \times \frac{w}{W} \times 100.$$

Examples.—1. The freezing-point of an aqueous solution of urea containing 2·9 gm. of urea per 150 c.c. solution is —0·6° C. Calculate the molecular weight of urea.

$$M = \frac{18·6}{0·6} \times \frac{2·9}{150} \times 100 = 60.$$

2. 0·346 gm. of a substance dissolved in 10·3 c.c. of water gave a depression of 0·921° C. Find its molecular weight.

3. 4·9818 gm. of cane sugar dissolved in 96·94 gm. of water gave a depression of 0·2795° C. Find its molecular weight.

4. 0·53 gm. of a solid dissolved in 51·5 gm. of benzene lowered the freezing-point of the latter by 0·61° C. Find the molecular weight of the solid.

Note.—The following rule should be adopted by students in calculating the molecular weights of substances in solution by the cryoscopic method. Examples may then be worked out without memorizing the formula given.

The Depression of the Freezing-point of a solvent by a solute is a Constant (K) when the concentration

is 1 Molar Weight (i.e. M = Molecular Weight) in 100 gm.* of the solvent. (K = cryoscopic constant.)

Example 1 above may then be worked as follows:

2·9 gm. of urea in 150 gm. of water give a depression of 0·6° C.

M gm. of urea in 150 gm. of water give a depression of $\dfrac{0\cdot6\times M}{2\cdot9}$ °C.

M gm. of urea in 100 gm. of water give a depression of $\dfrac{0\cdot6\times M}{2\cdot9}\times\dfrac{150}{100}$ °C.

Then

$$18\cdot6 = K = \frac{0\cdot6\times M}{2\cdot9}\times\frac{150}{100},$$

$$\therefore M = \frac{18\cdot6}{0\cdot6} + \frac{2\cdot9}{150}\times100 = 60.$$
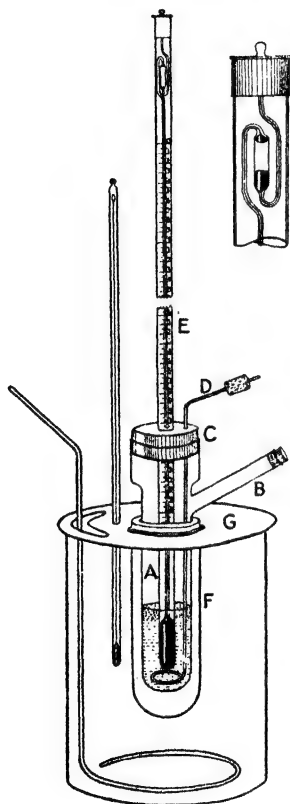
Fig. 5.—Beckmann's Freezing-point Apparatus

Beckmann's Apparatus (fig. 5) is used for the determination of the depression of the freezing-point of a solvent. It consists of a large tube A about 3 cm. in diameter, provided with a side-tube B. The tube A is closed with a cork C through which pass a stirrer D and a Beckmann thermometer E graduated to $\frac{1}{100}$°. A weighed quantity (about 25 gm.) of the solvent is placed in A, which is then fitted into a wider tube F; this serves as an air jacket, and prevents a too rapid change of temperature.

The apparatus is now introduced through a hole in the metal plate G into a vessel partly filled with a liquid, the

* Some authorities take 1000 gm. of solvent as standard.

temperature of which is about 5° lower than the freezing-point of the solvent. The solvent in A is constantly stirred; the thermometer rapidly falls, and sinks below the freezing-point of the solvent until the latter begins to freeze. The freezing-point of the solvent is taken when the thermometer becomes stationary. A weighed quantity of the substance is now introduced through the side tube B, and after the solute has been allowed to dissolve completely, the freezing-point of the solution is ascertained as before. The difference between the two freezing-points is the observed depression d; the molecular weight is then found by the above formula.

3. The Ebullioscopic Method.

Not only is the freezing-point of a solvent lowered when a substance is dissolved in it, but the boiling-point of a solvent is raised when a substance is dissolved in it.

The laws of elevation of the boiling-point are:

(*a*) The rise of boiling-point is proportional to the concentration, provided that the solutions are dilute.

(*b*) For a given solvent the same rise of boiling-point is produced by dissolving 1 gramme-molecule of any substance in a fixed quantity of solvent (Raoult's law).

The formula for the determination of molecular weight (M) by the elevation of the boiling-point is as follows:

$$M = \frac{K}{t} \times \frac{w}{W} \times 100,$$

where

    K is Elevation constant of the solvent for 100 gm.,
    w,   Weight of substance taken,
    t,   Observed elevation,
    W,   Weight of solvent taken.

The constant K differs from the constant employed in the cryoscopic method.

Solvent	Molecular elevation (K)	Boiling-point (B.P.)
Water	5·2	100° C.
Alcohol	11·5	78
Ether	21·0	35
Benzene	25·7	80·5
Chloroform	38·8	61·5
Acetic acid	25·3	118

Examples.—1. Calculate the molecular weight of cane sugar if the boiling-point of a 3 per cent aqueous solution is 100·045° C.

$$M = \frac{5·2}{0·045} \times \frac{3}{100} \times \frac{100}{1} = 347.$$

2. What is the molecular weight of a substance if the boiling-point of a solution of 3·7 gm. in 125 gm. of benzene is 0·44° C. above that of pure benzene?

Landsberger's Apparatus is used for the determination of the elevation of the boiling-point of a solvent. In this apparatus (modified by Walker and Lumsden), vapour from the flask A (fig. 6) passes into about 10 c.c. of the solvent in the vessel B and condenses there, its latent heat of evaporation raising the solvent to the boiling-point. The vessel is graduated, so that as soon as a steady boiling-point has been noted the volume of the solvent (which increases continuously) can be determined. Excess of vapour escapes through the orifice C and is condensed by the condenser D (not shown in the diagram). The weighed substance (about 0·5 gm.) is then introduced, and the boiling continued for about 5 min. The new boiling-point of the solution is noted, and the tube is immediately disconnected from the flask and the volume of the solution read off. The molecular weight of the substance is then calculated from the above formula.

Notes.—1. The liquid in the flask A must be the same as the solvent in B.

2. Steady boiling in the flask is essential, and is ensured by introducing pieces of porous pot.

3. The boiling is so conducted that the drops of liquid which condense fall slowly and regularly from the condenser.

4. A series of results can be obtained by the use of a single weighed quantity of solute by allowing more vapour to pass into the solution and recording the boiling-point of the solution, which is being continuously diluted.

5. The weight of the solvent is calculated by multiplying the volume recorded by its specific gravity. The solute content in most cases is so small that any alteration in the relative density of the solvent may be neglected.
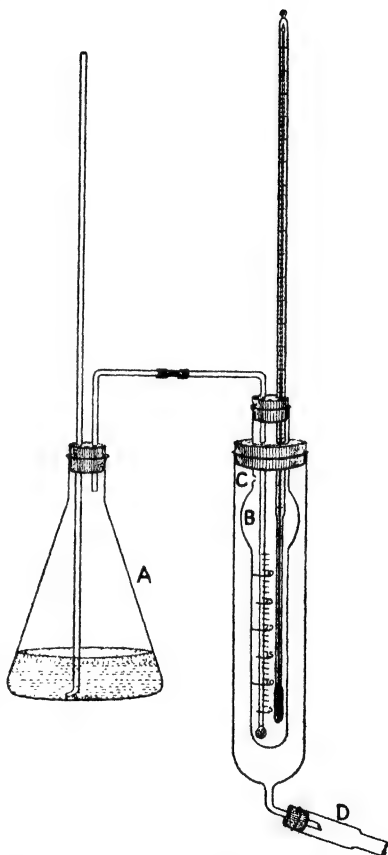
Fig. 6.—Landsberger's Boiling-point Apparatus (Modified by Walker and Lumsden)

The following rule should be adopted by students in calculating the molecular weights of substances in solution by the ebullioscopic method. Examples may

then be worked out without memorizing the formula given.

The Elevation of the Boiling-point of a solvent by a solute is a Constant (K) when the concentration is 1 Molar Weight (i.e. M = Molecular Weight) in 100 gm. of the solvent.

Example 1 above may then be worked as follows:

3 gm. of sugar in 100 gm. of water give an elevation of 0·045° C.

M gm. of sugar in 100 gm. of water give an elevation of $\dfrac{0·045 \times M}{3}$.

Then $\qquad 5·2 = K = 0·045 \times \dfrac{M}{3},$

$$\therefore\ M = \frac{5·2}{0·045} \times 3 = 347.$$

4. Osmotic Pressure Method.

Before discussing this method it is necessary to give a brief account of *osmosis* and *osmotic pressure*.

The terms solute, solvent and solution are so frequently used when describing the phenomenon of osmosis that a brief definition of each term will be given.

A solute is a substance which can dissolve in a solvent. These terms are interchangeable, the usage depending on the relative proportions. For example, salt can be dissolved in water, then salt is the solute and water the solvent; but it is equally correct, though less usual, to say that water is the solute and salt the solvent.

A solution is the product obtained when a solute dissolves in a solvent, and may be defined as a homogeneous mixture of two or more substances. This definition may be further extended to the solution of solids in solids, liquids in liquids, gases in solids, liquids in gases, &c.

Osmosis.

R. J. H. Dutrochet (1827) described an experiment in which a glass vessel was filled with copper sulphate solution and the opening was tightly closed with a bladder. When the whole was immersed in water, the contents of the vessel tended to increase, so that the bladder was stretched and eventually burst.

The Abbé Nollet had performed a similar experiment as
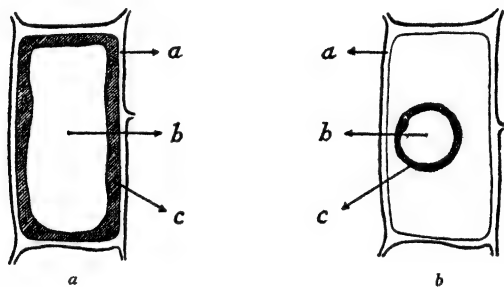
Fig. 7.—Vegetable cell to illustrate Plasmolysis (Osmotic Pressure)

early as 1748, using alcohol in the vessel. Similar observations were recorded by F. Parrot (1803) and by N. W. Fischer (1822), on the passage of water through a parchment membrane into solutions of copper sulphate, cane sugar, and alcohol.

Furthermore, it is well known that the cells of living plants and animals are usually surrounded by a membrane through which water can pass readily, and a knowledge of the action of solutions on plant structure is essential if we are to understand the principles underlying osmotic pressure.

Plant tissues consist of a number of small compartments, each of which with its contents is called a *cell*. Each cell (fig. 7a) has a wall composed of a substance called cellulose (*a*); the central portion consists of a watery liquid containing

dissolved substances, called the cell sap (*b*); between the cell sap and lining the cell wall is a layer called the primordial utricle (*c*), which consists of a semi-transparent gelatinous substance called *protoplasm*.

Pringsheim in 1854 noted that the protoplasmic contents of certain vegetable cells contract when placed in strong salt solution and shrink from the cell wall; at the same time the volume of the cell sap becomes less (fig. 7*b*). With a weaker solution of the salt the contraction is less, and in pure water no contraction takes place, and expansion, if any, cannot be observed, owing to the rigid outer cell wall, which is pervious both to water and to the substances in solution. The protoplasmic contents, then, are enclosed in a membrane which has the property of allowing pure water to pass but which is impervious to most dissolved substances. This phenomenon is known as **plasmolysis** and serves to determine osmotic pressure.

In *animals*, when red blood-cells or corpuscles are placed in water they rapidly swell and burst owing to the passage of water through the outer membrane into the cell; in a strong brine solution the red corpuscles shrivel up owing to the passage of water from the cell into the solution.

Experiment.—Pour a dilute solution (1 per cent) of cane sugar into a thistle funnel, the mouth of which is closed by pig's bladder or parchment. Immerse the funnel in a beaker of water: it will be observed that water passes through the parchment and the solution rises in the stem of the funnel. No sugar will be detected in the water outside the funnel (fig. 8).

Osmosis (Greek ὠσμύς (*osmos*), a push) **may be defined as the spontaneous flow of liquids through a partition or membrane.**

A membrane which allows the solvent to flow readily through it but is impermeable to the solute is said to be

a **semi-permeable membrane.** It may be regarded as a *molecular sieve* or *filter* allowing the passage of the molecules of the pure solvent but preventing the flow of any dissolved molecules. The passage of the solvent in a solution to the pure solvent outside can, however, take place only under the influence of a definite and often large pressure. Parchment paper is not a semi-permeable membrane for sugar and water, since it permits the flow of a little sugar. Up to 1867 the only semi-permeable membranes used were natural ones, such as pig's bladder and the primordial utricle of plant cells.

Moritz Traube in 1867 prepared a number of artificial semi-permeable membranes; the most efficient was copper ferrocyanide, $Cu_2[Fe(CN)_6]$, which was formed by the reaction of copper sulphate with potassium ferrocyanide as a reddish-brown gelatinous precipitate:

$$2CuSO_4 + K_4Fe(CN)_6$$
$$= Cu_2Fe(CN)_6 + 2K_2SO_4$$
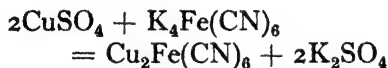
The artificially prepared semi-permeable membranes are slimy non-crystalline bodies called **colloids.** The name Colloid (Greek κολλα (*kolla*), glue) was originally given by Graham (1861). "Colloid" has come to mean a substance whose molecules are large in comparison with the pores of a parchment or artificial filter, such as glue, gelatine, gum, starch.
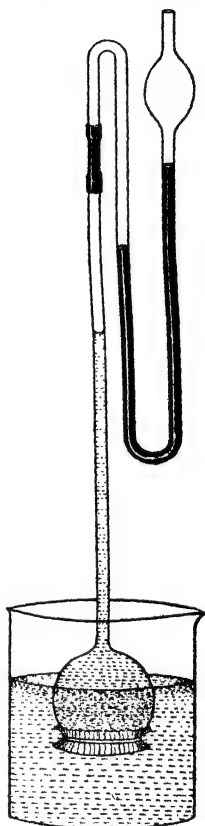
Fig. 8.—To illustrate Osmotic Pressure

Experiments.—(*a*) Nearly fill a boiling-tube with a dilute solution of potassium ferrocyanide, and carefully introduce by a small pipette a drop of a concentrated solution of copper sulphate. The drop becomes covered with a thin skin or membrane of copper ferrocyanide. The drop gradually increases in size owing to the passage of water from the dilute ferrocyanide solution into the stronger copper sulphate solution inside the drop. Place a bright light behind the tube and observe the streaks due to changes of concentration.

(*b*) Add a particle of solid ferric chloride to a dilute solution of potassium ferrocyanide; a Prussian blue film which gradually expands will be observed.

(*c*) Remove the shell of an egg with dilute hydrochloric acid. Place the egg in a strong brine solution and then in water. Observe that the egg contracts in the salt solution and expands when immersed in water.

(*d*) Place small pieces of the chlorides of ferric iron, nickel, cobalt, and copper in a concentrated solution of water-glass in a beaker. Observe the formation of pellicles which assume peculiar shapes on standing (" chemical garden ").

Osmotic Pressure.

In the experiment with the thistle funnel a column of liquid in the stem of the funnel is supported against the action of gravity. This column of water exerts a hydrostatic pressure downwards, due to its weight. With a given solution there is one pressure which just causes osmosis to cease; this is termed the **osmotic pressure** of the solution. The osmotic pressures of even moderately strong solutions are very high. Pfeffer found that a 1 per cent solution of cane sugar at $13 \cdot 5°$ C. produces an osmotic pressure of 521 mm. With more concentrated solutions abnormally high pressures have been recorded: a 17 per cent solution of ammonia at $0°$ C. can give a pressure of 224 atmospheres. Natural membranes and delicate artificial membranes cannot be used for such high pressures.

Measurement of Osmotic Pressure.

In order to register the magnitudes of osmotic pressures of solutions, Traube devised a method for strengthening semi-permeable membranes. A porous pot similar to those used in galvanic batteries is soaked in distilled water, then filled with potassium ferrocyanide solution and placed in a copper sulphate solution for some hours. Diffusion of the two solutions occurs and copper ferrocyanide is deposited in the pores of the pot. The pot is then washed in distilled water. Osmotic pressure is measured by filling the pot with a solution and fitting a manometer or pressure gauge into the open top: when the pot is immersed in a solvent there is a gradual rise of pressure in the manometer until a steady value is obtained. The hydrostatic pressure reduced to mm. of mercury indicates the osmotic pressure of the solution.

(a) W. P. F. Pfeffer made use of Traube's method for the preparation of an artificial semi-permeable membrane to conduct quantitative experiments on osmosis. He published his results in 1877 in a work entitled *Osmotische Untersuchungen.*

Pfeffer's apparatus is shown in fig. 9. The solution of cane sugar (which he used) is placed in a cylindrical porous pot which contains the semi-permeable membrane. The
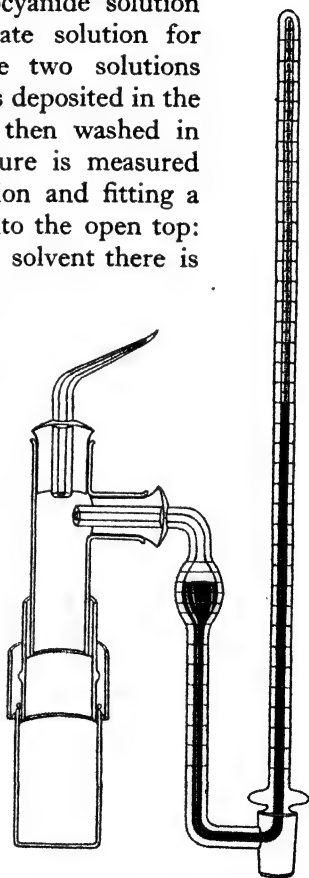
Fig. 9.—Pfeffer's Osmotic Pressure Apparatus

porous pot is fitted with a branched headpiece containing two ground-in stoppers. The side stopper is connected with a mercury manometer filled with nitrogen. The whole of the space between the mercury and the pot is filled with the solution, any excess being removed through the bent glass tube which passes through the vertical stopper and which is finally sealed off. When the pot is immersed in water the pressure inside slowly rises to a constant value. The magnitude of this pressure is determined from the difference in levels of the mercury in the right-hand graduated tube. Pfeffer's results are given on p. 27.

(*b*) H. de Vries between 1878 and 1888 conducted quantitative experiments on the protoplasmic contents of cells. He took as a standard the strength of a solution which was just sufficient to cause the primordial utricle to contract away from the cell walls, and showed that solutions of potassium nitrate, sodium nitrate, and potassium chloride produce the same contraction when their concentrations are in the ratio of their chemical or molecular equivalents; but with certain organic substances, such as cane sugar, invert sugar, and malic acid, a greater molecular concentration is required to produce the same contraction. Solutions which give the same contraction give the same osmotic pressure, and when such solutions are placed respectively inside and outside of a semi-permeable membrane, no pressure is recorded on a manometer. Solutions which act in this way are said to be **isotonic,** and from this the following law has been deduced.

The **Law of Isotonic Solutions** states that solutions of non-electrolytes which are isotonic with a given solution ,are isotonic with one another and contain the same number of gramme-molecules per litre. By means of this law the concentrations of solutions which are isotonic with one

another can be determined; for instance, red blood cor-
puscles placed in a 0·85 per cent solution of salt remain
unaltered, in weaker solutions they swell and burst, whilst
in stronger solutions they contract. The concentration of salt
in red blood corpuscles is thus 0·85 per cent, and a salt
solution of this strength is known in medicine and surgery
as a normal saline solution.

(c) Morse and Frazer. Good semi-permeable membranes
are most difficult to prepare and failures have been
numerous. Morse and Frazer between 1901 and 1909 con-
structed special pots from suitable clays which would give
the membrane sufficient support to withstand pressures up
to 300 atmospheres.

These pots were first soaked in water and air was ex-
cluded by evacuation. The cell was filled with a 2·5 per cent
solution of copper sulphate and immersed in a 3·7 per cent
solution of potassium ferrocyanide. An electric current was
then passed from a platinum electrode dipping into the
cell to a platinum cylinder surrounding it, the ions of $Cu^{..}$
and $[Fe(CN)_6]''''$ being deposited in the pores of the pot.
The electrical resistance of the cell increased as the mem-
brane was formed, until a maximum was reached. The
current was then stopped, the cell washed with distilled
water, and the process repeated until all the pores had been
filled (this was tested by a sugar solution). Many months
sometimes elapsed before a good membrane was obtained.

Morse and Frazer measured ordinary osmotic pressure
with a gauge similar to that used by Pfeffer, but higher
osmotic pressures were determined by observing the
change of refractive index with compression by means of
an interferometer.

(d) Berkeley and Hartley. Between 1904 and 1919 the Earl
of Berkeley and Mr. E. G. J. Hartley experimented with solu-
tions of sugars and other substances which were impervious to
a membrane of copper ferrocyanide. The method adopted

by these scientists was to apply to a solution a pressure which was just sufficient to stop osmosis.

Their apparatus (fig. 10) consisted of a porous cylinder A containing the copper ferrocyanide in its walls. The inside
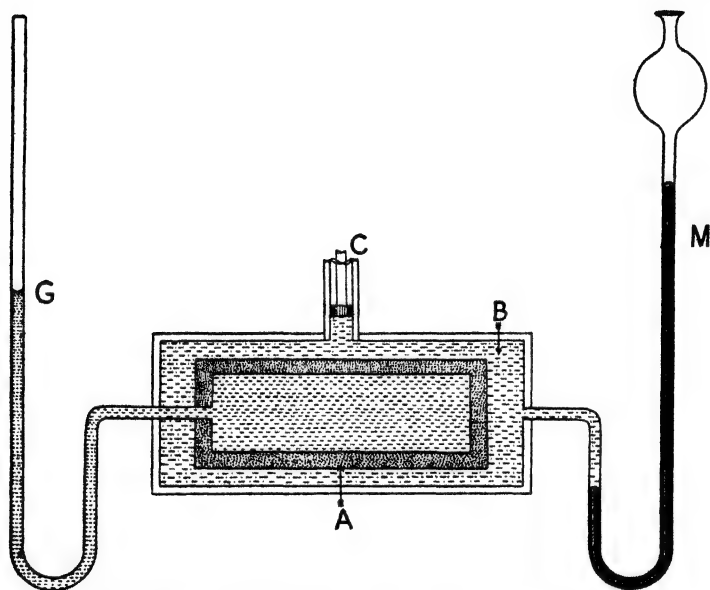
Fig. 10.—Berkeley and Hartley's Osmotic Pressure Apparatus (Diagrammatic)

of this cylinder contained water, and was connected to a water manometer G.   The annular space B outside the cylinder contained the solution.   Water tended to pass through the pot, but this was prevented by hydraulic pressure applied to the solution through the tube C and measured by a gauge, the correct osmotic pressure being taken as the mean of two readings recorded on the mercury manometer M when the water level in the gauge G just moved vertically up and then down.

Laws of Osmotic Pressure.

Pfeffer in 1877 obtained the following results with dilute solutions of cane sugar; in order to show how the Laws of Osmotic Pressure have been derived, the ratios of the pressure and absolute temperature are included.

TABLE I.   OSMOTIC PRESSURE OF ONE PER CENT CANE SUGAR SOLUTIONS

Temperature	0	6·8	13·7	14·2	15·5	22	32	36
Absolute Temp. T	273	279·8	286·7	287·2	288·5	295	305	309
Pressure P (mm.)	648	664	691	671	684	721	716	746
Ratio P/T	2·37	2·37	2·41	2·34	2·37	2·44	2·35	2·41

TABLE II.   OSMOTIC PRESSURE OF SUGAR SOLUTIONS AT 0° C.

Concentration (C) grammes of sugar in 1 litre of solution	Osmotic Pressure in atmospheres (P)	Ratio P/C
10·03	0·686	0·068
20·14	1·34	0·067
40·60	2·75	0·068
61·38	4·04	0·066

Van't Hoff in 1887 showed that the osmotic pressure of a substance in solution exhibits close analogies with the pressure of a gas.

Law I.   Osmotic pressure is directly proportional to the absolute temperature.

This is obvious from Pfeffer's results (Table I), P/T being constant.   It has also been confirmed by the more recent experiments of Morse and Frazer with a solution containing 0·3 gm. molecules of sugar per 1000 gm. of water.

TABLE III.   VARIATION OF OSMOTIC PRESSURE WITH TEMPERATURE

$t°$ C.	0°	10°	20°	25°
T° absolute	273	283	293	298
P in atmos.	7·085	7·334	7·605	7·729
P/T	0·02595	0·02591	0·02596	0·02594

Law II.   Osmotic pressure is directly proportional to the concentration of the solution for the same solute in the same solvent and at constant temperature.

That is, the osmotic pressure varies inversely as the volume of the solution in which a given weight of sugar is dissolved. By Pfeffer's results (Table II), P/C is a constant. More accurate results by Morse and Frazer for cane sugar have confirmed this.

TABLE IV.   OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS
(MORSE AND FRAZER)

Concentration (gm.-mols. in 1000 gm. of water)	Mean Osmotic Pressures in Atmospheres					
	0° C.	5°	10°	15°	20°	25°
0·1	2·462	2·452	2·498	2·541	2·590	2·634
0·2	4·722	4·818	4·893	4·985	5·064	5·148
0·3	7·085	7·198	7·334	7·476	7·605	7·729
0·4	9·442	9·608	9·790	9·949	10·137	10·296
0·5	11·895	12·100	12·297	12·549	12·748	12·943
0·6	14·381	14·605	14·855	15·144	15·388	15·624
0·7	16·886	17·206	17·503	17·815	18·128	18·434
0·8	19·476	19·822	20·161	20·535	20·905	21·252
0·9	22·118	22·478	22·884	23·305	23·717	24·126
1·0 = 342	24·825	25·283	25·693	26·189	26·638	27·053

From these results, for a given temperature the osmotic pressure is proportional to the concentration; that is, P/C is a constant.   For 0° C. the constant is 24·107.

If P represents the osmotic pressure and V the volume

of solution containing one gramme-molecule of the dissolved substance (this volume is calculated by dividing 342, the molecular weight of cane sugar ($C_{12}H_{22}O_{11}$), by the concentration per litre), the following table gives the values of PV from the results of Berkeley and Hartley. It is clear that PV is a constant.

TABLE V. OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 0° C.

Concentration in grammes per litre	Osmotic Pressure (P) in atmospheres	Volume (V) in litres	Product P × V
2·02	0·134	169·3	22·7
10·00	0·66	34·2	22·6
20·00	1·32	17·1	22·6
45·00	2·97	7·60	22·6
93·75	6·18	3·65	22·6

Law III. Osmotic pressure is the same for all solutions of non-electrolytes which contain the molecular weight in grammes of the solute in the same volume of solvent, provided the temperature remains constant.

The standard volume taken is 22·4 litres, in order that a comparison may be made with Avogradro's hypothesis and the gas laws. For example, if 342 gm. of cane sugar or 60 gm. of urea are dissolved in 22·4 litres of water, the solutions exert an osmotic pressure of 760 mm. at 0° C.

From the results of the above experiments an osmotic equation exactly similar to that used for gases can be expressed as follows:

Since

$$P \propto T \text{ if V is constant}$$

and

$$P \propto \frac{1}{V} \text{ if T is constant,}$$

we have $\quad P \times V = \dot{R}T \quad \text{or} \quad \frac{PV}{T} = \dot{R}$, a constant.

Van't Hoff showed that the constant $\dot{R}$ has the same value as the constant of the gas equation, which for ideal gases is 0·0821 in litre-atmospheres per gramme-molecule. From Berkeley and Hartley's data, the equation

$$PV = \dot{R}T$$

gives $$22·6 = \dot{R} \times 273,$$

whence $\dot{R} = 0·0828$, in close agreement with the value found for gases.

These relations may be summarized in the following law, known as Van't Hoff's Gaseous Theory of Solution:

The osmotic pressure of a dilute solution is equal to the pressure which the dissolved substance (i.e. the solute) would exert if it were a gas at the same temperature and occupying the same volume as the solution.

Osmotic Pressure of Concentrated Solutions.

The osmotic equation $PV = \dot{R}T$ holds good only for very dilute solutions. For concentrated solutions PV increases rapidly with rise of osmotic pressure. The results of Frazer and Lotz in the following table illustrate this divergence, which is analogous to that of gases at high pressures.

TABLE VI.   OSMOTIC PRESSURES OF CONCENTRATED SOLUTIONS
OF CANE SUGAR AT 30° C.

Concentration		Osmotic Pressure				
Grammes per 1000 c.c. of solution	Grammes per 1000 gm. of water	P	V	PV	V'	PV'
478·3	680	57·5	0·715	41·1	0·503	28·9
605·4	980	90·4	0·565	51·1	0·349	31·5
700·2	1260	129·5	0·488	63·2	0·271	35·1
781·4	1549	169·1	0·438	74·1	0·221	37·4
839·8	1796	206·1	0·407	83·9	0·190	39·2

In this table two results are given, depending upon the concentrations in grammes (*a*) per litre of solution, (*b*) per 1000 gm. of water. The latter expresses the view of some scientific workers that in comparing osmotic pressures the solutions should be made " weight normal " instead of " volume normal ". Although the value PV′ more closely approaches the theoretical value, it is still too great.

In stronger solutions the size of the molecules and their mutual attraction must be considered; van der Waals' equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = \dot{R}T$$

should be used, where *a*, *b* are constants. For the explanation of this formula, works on Physical Chemistry should be consulted.

Determination of Molecular Weight by Osmotic Pressure.

We now revert to the question of the determination of molecular weight by the osmotic pressure method.

The extension of Avogadro's hypothesis to solutions may be expressed as follows: Equal numbers of molecules in equal volumes of solvent, that is, equal molecular concentrations, exert equal osmotic pressures if the temperature is constant. In other words, the molecular weight of a non-electrolyte is the number of grammes of it which, when dissolved in 22·4 litres of a solvent, will produce a solution having an osmotic pressure of 760 mm. at 0° C. From the above data it is possible to obtain a formula for the determination of molecular weights of non-electrolytes.

Since

$$PV = \dot{R}T$$

and

$$\frac{V}{\prime} = \frac{\text{Molecular weight}}{\text{Weight taken per litre}} = \frac{M}{S}$$

we have

$$M = \frac{\dot{R} \times T \times S}{P}.$$

Example 1.—The osmotic pressure of a solution containing 2·5 gm. of urea per 500 c.c. is 2·04 atmospheres at 25° C.; calculate the molecular weight of urea.

S, the weight of substance per litre, is 5;

$$M = \frac{0 \cdot 0821 \times 298}{2 \cdot 04} \times 5 = 60 \text{ (approx.)}$$

$$\left(\text{or} \quad \frac{1 \times 22 \cdot 4}{273} \times \frac{298}{2 \cdot 04} \times 5 \right).$$

Example 2. *Method* 1.—Calculate the osmotic pressure of a solution of cane sugar containing 9·5 gm. of sugar in 120 c.c. of solution at 15°.

$$S = \frac{9 \cdot 5}{120} \times 1000$$

$$P = \frac{\dot{R} \times T \times S}{M}$$

$$= \frac{0 \cdot 0821 \times 288}{342} \times \frac{9 \cdot 5 \times 1000}{120}$$

$$= 5 \cdot 47 \text{ atmospheres.}$$

Method 2.—Since 9·5 gm. of sugar are dissolved in 120 c.c., 342 gm. of sugar will dissolve in 4·32 litres to give a solution of the same strength.

Now 1 gm. molecule in 22·4 litres at 273° abs. gives an osmotic pressure of 1 atmosphere,

∴ 1 gm. molecule in 4·32 litres at 273° abs. gives $\dfrac{22·4}{4·32}$ atmospheres, and 1 gm. molecule in 4·32 litres at 288° abs. gives

$$\frac{22·4}{4·32} \times \frac{288}{273} = 5·47 \text{ atmospheres.}$$

Note.—The following definition of Osmotic Pressure (O.P.) should be adopted by students when calculating the molecular weights or osmotic pressures of substances in solution. Examples may then be worked out without memorizing the formulæ given.

The Osmotic Pressure of a solute in a solvent is 1 atmosphere at 0° C. when the concentration is 1 Molar Weight (i.e. molecular weight) in 22.4 litres of solvent.

Example 1 above may then be worked as follows:

O.P. is 2·04 atmos. at 25° C. for a solution containing 2·5 gm. in 500 c.c.

O.P. is 2·04 atmos. at 0° C. for a solution containing 2·5 gm. in $500 \times \dfrac{273}{298}$ c.c.

O.P. is 1 atmos. at 0° C. for a solution containing $\dfrac{2·5}{2·04}$ gm. in $500 \times \dfrac{273}{298}$ c.c.,

i.e. containing $\dfrac{2·5}{2·04} \times \dfrac{298}{273} \times \dfrac{22,400}{500}$ gm. in 22·4 litres (approximately 60 gm.).

∴ Molecular weight of urea = 60.

Example 2 may be worked in the same way.

Nature or Cause of Osmotic Pressure.

Various investigators have explained Osmotic Pressure as:

1. Due to the bombardment of solute molecules: the solvent molecules are capable of passing a semi-permeable membrane, which acts like a sieve and prevents the passage of the larger solute molecules. This view is supported by the fact that an osmotic pressure can be produced by immersing a mixture of propyl alcohol and water either in propyl alcohol or in water.

2. Due to an attraction between solute and solvent, which tend to form hydrates, e.g. $C_{12}H_{22}O_{11} \cdot 5H_2O$.

3. Due to physical causes, e.g. expansion or diffusion of the solute. The solvent dissolves in the semi-permeable membrane and then passes through it in either direction, whereas the solute is insoluble.
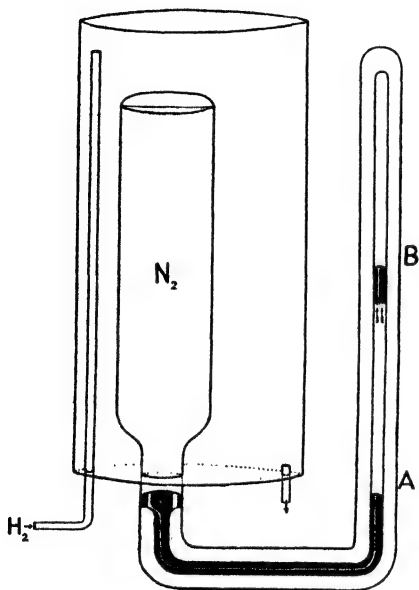
Fig. 11.—Ramsay's Osmotic Pressure Apparatus for gases

This latter view is upheld by Ramsay, by an experiment in which palladium forms a semi-permeable membrane for a mixture of gases. Nitrogen is contained in a palladium bulb heated to 300° C. and connected to a manometer (fig. 11). The bulb is encased in a vessel filled with hydrogen at atmospheric pressure. The hydrogen dissolves in the

palladium and diffuses through it, but the nitrogen does not. The increased pressure inside the bulb is shown on the gauge (A to B) and may be called the " osmotic pressure " of nitrogen, hydrogen being the solvent and nitrogen the solute. This view can also be illustrated with phenol, which acts as a semi-permeable membrane with the solvent water, but is impervious to a solution of calcium nitrate. The molecules of water can either dissolve in or diffuse through phenol, but the calcium nitrate molecules cannot.

Note.—It must be made clear, however, that at the present time the various views and theories offered as to the true cause of osmotic pressure or the mechanism by which osmotic pressure is produced have not been corroborated; but the bombardment hypothesis forms the simplest basis for the mathematical analysis of the phenomenon.

5. Lowering of Vapour Pressure Method.

Liquids tend to vaporize and in so doing exert a pressure known as the *vapour pressure*, which acts in a direction opposite to that of the atmosphere. This may be illustrated by taking two barometer tubes about 80 cm. long, filling them with mercury, and inverting them in a mercury reservoir. The barometer height is noted. Into one tube a few drops of water are introduced and into the other a few drops of ether. These solvents vaporize in the Torricellian vacua and the mercury is depressed. By noting the mercury levels the vapour pressures of the two liquids at atmospheric temperature are found. It will be observed that the effect of the ether is much greater than that of the water. The vapour pressure of a liquid rises rapidly with the temperature, as is shown by the table of vapour pressures of water (Appendix, p. 637).

When a solvent is admitted into the Torricellian vacuum

in a barometer tube the mercury is depressed in accordance with the vapour pressure of the solvent at a stated temperature. If, however, a solution of a solute in the solvent is admitted, the depression of the mercury is lessened, and this relative lowering of the vapour pressure is directly proportional to the concentration of the solute. From the results of numerous experiments the following law has been formulated.

Raoult's Vapour Pressure Law.

The relative lowering of the vapour pressure for a given solvent at a fixed temperature is proportional to the concentration of the solute (provided that the solution is dilute), and is equal to the ratio of the number of molecules of solute and of solvent in the solution. This law may be expressed mathematically as follows:

$$\frac{p_0 - p_s}{p_0} = \frac{n}{N + n}$$

where p_0 is the vapour pressure of the solvent, p_s the vapour pressure of the solution, n the number of molecules of solute, and N the number of molecules of solvent.

From this law it is possible to deduce a formula for determining the molecular weight of a substance in a solution by the lowering of the vapour pressure of the solvent. From experimental results it is found that

The lowering of the vapour pressure in millimetres of a boiling solvent, caused by one grammemolecule of a non-volatile solute in one litre of solution, is a constant (K) for that particular solvent.

The values of the constant K, the molecular lowering

of vapour pressure, for some common solvents at standard pressure are as follows:

Solvent	K	Solvent	K
Water	202·5	Acetone	1061
Carbon disulphide	526·6	Benzene	1214
Chloroform	620·4	Ethyl acetate	1320
Alcohol	871·5	Ether	1577

Let M be Molecular weight of the substance;
    K,   Molecular lowering of vapour pressure;
    w,   Weight of substance taken;
    p,   Observed lowering of vapour pressure in mm.;
    V,   Volume of solvent taken;
    H,   Barometer height in mm.

Then w gm. dissolved in V c.c. give p mm. vapour pressure lowering;

M gm. dissolved in V c.c. give $p \times \dfrac{M}{w}$ mm.;

M gm. dissolved in 1000 c.c. give

$$p \times \frac{M}{w} \times \frac{V}{1000} \text{ mm. at standard pressure,}$$

or

$$p \times \frac{M}{w} \times \frac{V}{1000} \times \frac{760}{H} \text{ mm. with barometer at height H,}$$

since the greater the atmospheric pressure, the smaller the lowering of the vapour pressure; then

$$K = p \times \frac{M}{w} \times \frac{V}{1000} \times \frac{760}{H},$$

$$\therefore M = K \times \frac{1000 \times w \times H}{p \times V \times 760}.$$

Example.—0·25 gm. of *p*-nitrotoluene was dissolved in 20 c.c. of acetone and gave a lowering of the vapour pressure of 9·65 cm. at standard pressure. Find the molecular weight of the substance.

$$M = \frac{1061 \times 1000}{96 \cdot 5} \times \frac{0 \cdot 25}{20} = 137 \cdot 4.$$

Note.—The following rule should be adopted by students when calculating the molecular weight of dissolved substances by the lowering of vapour pressure method. Examples may then be worked out without memorizing the formula given.

The Lowering of the Vapour Pressure of a solvent by a solute is a Constant (K) when the concentration is 1 Molar Weight in 1000 c.c. of the solvent.

The example above may then be worked as follows:

Lowering of V.P. is 96·5 mm. when 0·25 gm. is dissolved in 20 c.c.

Lowering of V.P. is $\dfrac{96 \cdot 5}{0 \cdot 25} \times M \times \dfrac{20}{1000}$ when M gm. are dissolved in 1 litre.

$$\therefore K = \frac{96 \cdot 5}{0 \cdot 25} \times M \times \frac{20}{1000};$$

but K (for acetone) is 1061 mm.,

$$\therefore M = 137 \cdot 4.$$

Lowering of Vapour Pressure: Menzies' Method.

Menzie's Method is one of the best methods for the determination of the molecular weight of a substance by the lowering of the vapour pressure.

The apparatus consists of an outer boiling-tube A which contains the solvent and is attached to a reflux condenser R (fig. 12). The inner tube B is fitted into the neck of A by

means of a ground glass joint D. The tube B contains the solution; the tube is graduated in cubic centimetres, and into its wall is sealed a narrow gauge tube graduated in millimetres, the lower closed end of which is perforated by a number of holes. The neck of the inner tube B can be closed by a ground stopper S.

Procedure.—In order to explain the manipulation of this apparatus the determination of the lowering of the vapour pressure of *p*-nitrotoluene in acetone will be discussed. Half fill the outer boiling-tube with pure acetone, close the tube by means of the stopper S, and boil vigorously for ten minutes to remove dissolved gases. The screw clip C must be open in order to permit the condensed vapours to return to the tube A.   Replace B without the stopper, close the clip C and boil the acetone in A for a minute or two; the vapour bubbles through the liquid in B. The stopper is now warmed by placing it loosely in the neck of the inner tube, and is then inserted into the neck, and at the same moment the clip C is opened. The boiling is continued for a few minutes and the zero reading is taken both
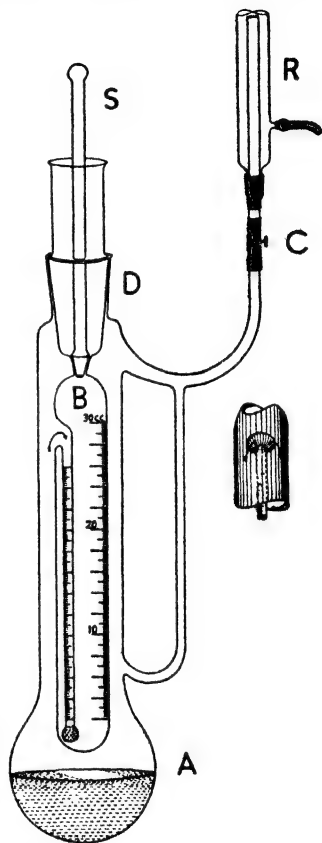
Fig. 12.—Menzies' Apparatus: Lowering of Vapour Pressure

in the graduated inner tube and in the gauge tube. These readings should be approximately the same, although the level in the gauge tube is usually a little higher owing to

capillary attraction. The stopper is now removed, and a weighed pellet of *p*-nitrotoluene (about 0·25 gm.) is introduced into B. The solvent is boiled and the vapour allowed to bubble through the solution as described above. The stopper is replaced and after ten minutes the readings are again taken and corrected for the zero reading. Since the solution has a lower vapour pressure than the solvent the level in the gauge tube will be below the level of the liquid in the tube B. The difference in reading (9·65 cm.) gives the lowering of the vapour pressure. The volume of the acetone is then read off (20 c.c. in the example given). The M.W. of *p*-nitrotoluene is then calculated as already described.

Repeat, using

1. Cane sugar or urea as solute and water as solvent.
2. Iodine as solute and ether as solvent.
3. Sulphur as solute and carbon bisulphide as solvent.

(B) Chemical Methods

The Chemical Methods employed for the determination of molecular weights may be subdivided into methods applied to (*a*) organic acids, (*b*) organic bases, (*c*) neutral compounds.

(*a*) Organic Acids.

These are estimated by conversion into silver salts, which are obtained in the form of insoluble precipitates. These salts are filtered off and dried. A weighed portion is then ignited and the weight of the metallic residue of silver determined. From the results obtained the molecular weight can be estimated, provided the basicity of the acid is known.

Example.—About 2 gm. of acetic acid are weighed out into a conical flask, excess of ammonia is added, and the solution boiled until free from the smell of ammonia. The

liquid is tested from time to time until neutral to litmus. The flask is then cooled and excess of silver nitrate solution added. The precipitate formed is filtered off through a porcelain funnel by a suction pump, is well washed and removed to a porous plate and placed in a vacuum desiccator to dry, preferably in the dark, since silver salts are decomposed by light. When the precipitate is thoroughly dry about 0·25 gm. is weighed out into a weighed porcelain crucible, covered with a lid and heated gently over a small flame. After the first reaction is over the temperature is raised and the heating continued at a dull red heat for 15 min. The crucible is cooled in a desiccator and weighed. It is then reheated, cooled and weighed until the weight is constant.

Let   W be Weight of salt taken,
                N,   Basicity of acid,
                w,   Weight of silver,
                M,   Molecular weight of acid;

then the molecular weight of the acid may be calculated from the formula

$$M = \left[\frac{W \times 108}{w} - 108\,N \right] + N.$$

Explanation of formula for a monobasic acid (e.g. acetic acid). Acetic acid has the formula CH_3COOH and basicity 1, and the formula for silver acetate is CH_3COOAg.

If the molecular weight of acetic acid is M it is obvious that the molecular weight of silver acetate can be obtained by subtracting the weight of one hydrogen atom (i.e. N) from M and adding the weight of one silver atom (N times the weight of the silver atom), namely, 108. That is,

Molecular weight of silver acetate = M − 1 + 108.

Now if w gm. of silver are obtained from W gm. of the

silver salt, then 108 gm. of silver are obtained from $\dfrac{W}{w} \times 108$ gm. of the silver salt, but this is equivalent to $M - 1 + 108$,

$$\therefore M - 1 + 108 = \frac{W}{w} \times 108$$

or

$$M = \left[\frac{W \times 108}{w} - 108 \right] + 1.$$

Similarly, if the acid is dibasic 2×108 (i.e. 2 silver atoms) must be subtracted and 2 (i.e. 2 hydrogen atoms) added, and again, if the acid has basicity N the formula becomes that shown above.

(b) Organic Bases.

These substances, e.g. aniline, brucine, strychnine, quinine, combine with hydrochloric acid to form salts which, like ammonium chloride, form double salts with platinic chloride and auric chloride of the general formula

$$R_2^{\cdot}H_2PtCl_6; \quad R^{\cdot}HAuCl_4,$$
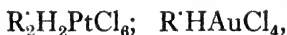
where $R^{\cdot}$ is a molecule of a monacid base. When these salts are ignited in a porcelain crucible pure platinum and gold remain. By estimating the weight of platinum obtained from a known weight of the base, the molecular weight of the base can be calculated.

Procedure.—Dissolve about a gramme of pure aniline in 10 c.c. of a mixture of equal volumes of concentrated hydrochloric acid and water. Excess of platinic chloride is then added to the clear hot solution; on cooling, a yellow crystalline precipitate of the chloroplatinate $(C_6H_5NH_2)_2 \cdot H_2PtCl_6$ separates out. Filter on the porcelain funnel.

Wash the precipitate with strong hydrochloric acid (water must not be used, as this chloroplatinate is very soluble in

water; most chloroplatinates, however, are insoluble in water). Remove the precipitate to a porous plate and dry over solid caustic potash in a vacuum desiccator. When the substance is quite dry weigh out about 0·5 to 1 gm. in a weighed crucible with a lid and heat gently at first, finally raising the temperature to decompose the salt. Cool in a desiccator and weigh. Reheat and weigh until the weight is constant.

Calculation.

Let molecular weight of base be M. Then molecular weight of salt $= 2M + 410$, since molecular weight of H_2PtCl_6 is 410.

Let weight of platinum obtained be w gm. and weight of salt taken W gm.

Since w gm. of platinum are obtained from W gm. of salt, 195·23 gm. platinum are obtained from $\dfrac{W}{w} \times 195\cdot23$ gm. of salt;

$$\therefore 2M + 410 = \frac{W}{w} \times 195\cdot23,$$

$$M = \frac{\left(\dfrac{W}{w} \times 195\cdot23\right) - 410}{2}.$$

Example 1.—0·8516 gm. of aniline chloroplatinate gave 0·279 gm. of platinum. Find the molecular weight of aniline.

Molecular weight of salt $= \dfrac{0\cdot8516 \times 195\cdot23}{0\cdot279} = 595\cdot9.$

Molecular weight of aniline $= \dfrac{595\cdot9 - 410}{2} = 92\cdot95.$

Calculated result $= 93\cdot06.$

Example 2.—The platinum double salt of an organic

base contains 37 per cent of platinum. What is the molecular weight of the base?

37 parts of platinum are contained in 100 parts of salt,
195·23 ,,   ,,   ,,   ,,   ,,   527·6 ,,   ,,

Molecular weight of salt = 527·6,

∴ Molecular weight of base (mon-acid base only)

$$= \frac{527·6 - 410}{2}$$

$$= 58·8,$$

which corresponds to (C_3H_9N).

(c) Neutral Organic Compounds.

These are estimated by preparing their derivatives, and examining the replaceable hydrogen from the compounds produced.

Chlorine, for instance, can act on naphthalene to form the derivative monochloro-naphthalene, which has the following composition:

Carbon,	73·8 per cent.
Hydrogen,	4·3 per cent.
Chlorine,	21·9 per cent.

This corresponds to the formula $C_{10}H_7Cl$, indicating that one of the hydrogen atoms of naphthalene, $C_{10}H_8$, has been replaced by one chlorine atom.

Example.—0·427 gm. of naphthalene on treatment with chlorine was converted into 0·5417 gm. of monochloro-naphthalene containing 21·9 per cent of chlorine. Find the molecular weight of naphthalene.

Let M be the molecular weight of naphthalene.

Since 0·427 gm. of naphthalene gives 0·5417 gm. of the chloro-compound,

$$\text{Mol. Wt. of chloro-compound} = \frac{0 \cdot 5417}{0 \cdot 427} \times M.$$

Now 21·9 parts of chlorine are contained in 100 parts of the chloro-compound,

$$\therefore 35 \cdot 5 \text{ parts of chlorine are contained in } \frac{100}{21 \cdot 9} \times 35 \cdot 5$$

parts of the chloro-compound,

$$\therefore \frac{0 \cdot 5417}{0 \cdot 427} \times M = \frac{100}{21 \cdot 9} \times 35 \cdot 5,$$

$$\therefore M = \frac{100}{21 \cdot 9} \times 35 \cdot 5 \times \frac{0 \cdot 427}{0 \cdot 5417} = 127 \cdot 8.$$

Calculated result = 128.

Molecular Weights of Colloids

An ordinary solution consists of a solute which is molecularly dispersed in a solvent; that is, the solute is broken down completely into molecules and in some cases into ions. Such substances were called **crystalloids** by Graham. It frequently happens, however, that the substance does not disperse molecularly; instead, numerous molecules aggregate together and disperse themselves in a solvent. These " aggregated " molecules sometimes pass through a filter paper; they are too small, however, to be seen under a microscope. Such substances, e.g. starch, albumin, glue, invertase, hæmoglobin, gelatine, pepsin, are known as **colloids** (p. 21). They are difficult to crystallize.

The osmotic pressures of colloids are very small and give very high figures for the molecular weights. Many proteins have a molecular weight of 17,600; others, e.g. haemo-cyanins, have a molecular weight of the order of 10^6.

Although the osmotic pressure method, the depression of the freezing-point method and other methods have been used in the determination of the molecular weights of colloids, the ultra-centrifuge method of Svedberg (Upsala, 1928) gives the best result. Here the relationship between the concentration of colloidal particles at two levels in a cell for a given speed (some 65,000 r.p.m.) of the centrifuge is determined.

The method is based on the fact that the size of a particle can be determined by the rate with which it falls through a medium (i.e. a solvent in this case). The colloidal solution in the cell used in the centrifuge is photographed at definite intervals and compared with standard photographs of solutions of known concentration. The molecular weight is then determined from a standard calculated formula.

Further details are given in Appendix II, p. 647. Students interested in the subject should read Svedberg, *Colloid Chemistry*, (Chemical Catalog Co., New York, 1928), pp. 146–180; *Science Progress*, No. 123, pp. 534–536; *Nature*, Vol. 139, pp. 1051–62 (1937).

QUESTIONS

1. 0·177 gm. of an organic compound (A) when boiled with an excess of an aqueous solution of sodium hydroxide evolved ammonia which neutralized 30·0 c.c. of 0·1 N sulphuric acid. From the solution remaining after all the ammonia had been evolved, the silver salt of a monobasic organic acid containing 14·4 per cent of carbon, 1·80 per cent of hydrogen, and 64·7 per cent of silver was obtained. Give the name and constitutional formula of the compound (A).

$$(H = 1, C = 12, N = 14, O = 16, Ag = 108)$$

(Pre. Med.)

2. The combustion analysis of an aromatic sulphur compound yielded the following results: 0·1025 gm. gave 0·2679 gm. CO_2 and 0·0459 gm. H_2O. Calculate possible molecular compositions for the substance. C = 12; O = 16; S = 32.

3. Calculate the empirical formula of an organic compound containing only carbon, hydrogen and oxygen, if 0·24 gm. on combustion gave 0·33 gm. of carbon dioxide and 0·27 gm. of water. What further experimental data would you require in order to decide upon the molecular formula?   (*Prel. Sc.*)

4. Calculate the molecular formula of an organic substance from the following data: Carbon, 60·8 per cent; Hydrogen, 15·3 per cent; Nitrogen, 23·8 per cent; vapour density, 30.

5. Describe Victor Meyer's method of determining the vapour density of a liquid, e.g. chloroform. From the following data calculate the vapour density of an unknown organic liquid:

Barometer   ..   ..   718·3 mm.
Tension of aqueous vapour at 14° C.   ..   11·91 mm.
Temperature of air displaced   ..   ..   14° C.
Weight of substance taken ..   ..   ..   0·16175 gm.
Volume of air measured at 14° C. ..   ..   16·2 c.c.

6. Write a brief account of the cryoscopic (freezing-point) method for the determination of the molecular weights of non-electrolytes, using (*a*) water, (*b*) benzene as the solvent.

The freezing-point of 60 gm. of benzene was found to be 5·5° C. After the addition of 1 gm. of a substance the freezing-point fell to 4·72° C. The molecular depression for 100 gm. of benzene is 50. Calculate the molecular weight of the substance.

7. A volatile ester of an organic acid contains 49·3 per cent of carbon and 6·85 per cent of hydrogen. The vapour density as determined by Victor Meyer's method is approximately 73 (H = 1). Calculate the molecular formula of the ester. Outline the experiments you would perform to determine the nature of the ester.

8. The analysis of an organic compound gave the following result: Carbon, 62·07 per cent; Hydrogen, 10·34 per cent.

A vapour density determination gave the value 28.

Calculate the molecular formula for the compound and suggest a structural formula for it.

9. Describe, with experimental details, how the molecular weight of a dissolved substance may be found from the depression of the freezing-point of a solvent.

Two solutions containing, respectively, 7·5 gm. of urea (CON_2H_4) and 42·75 gm. of a substance X in 1000 gm. of water, freeze at the same temperature. Calculate the molecular weight of X.

(Higher School Cert.)

10. The analysis of a substance gave the following results by weight: C, 52·3%; H, 13%; O, 34·7%.

In a Victor Meyer determination 0·079 gm. gave 38 c.c., corrected to S.T.P., of vapour. What is the probable formula of the substance? (H = 1; C = 12; O = 16).

11. Write down the possible structural formulæ of a substance containing carbon, hydrogen, and oxygen, given the following data:

(1) 0·29 gm. when oxidized by copper oxide yielded 0·66 gm. of carbon dioxide and 0·27 gm. of water.

(2) 1·45 gm. dissolved in 500 gm. of acetic acid depressed the freezing-point from 16·750° C. to 16·560° C. The molecular lowering for 1000 gm. of the solvent is 3·9° C.

What further evidence would you require before you made a choice of one of these formulæ?

(Civil Service: Executive Group).

12. How would you determine the percentages of carbon and hydrogen in an organic substance?

The following figures were obtained in an actual analysis, and no other elements could be found by qualitative analysis; find the empirical formula of the substance. C = 4·48%, H = 0·74%, I = 94·78%. (Atomic weights: C = 12, I = 127).

13. The analysis of an organic compound gave the following result: Carbon, 39·95 per cent; Hydrogen, 6·69 per cent.

A vapour density determination gave the value 59·5.

Calculate the molecular formula of the compound and suggest a structural formula for it.

14. A combustion experiment and a vapour density determination showed that a certain organic liquid had the molecular formula C_2H_6O.

What structural formulæ may it possess?

Describe the experiments by which you would identify it.

(Civil Service:—Navy, Army and Air Force.)

15. The analysis of an organic compound gave carbon 54·54 and hydrogen 9·09 per cent. The vapour density was found to be 21·5. Calculate the molecular formula for the substance and suggest a structural formula for it.

16. What is the relation between the molecular weight and the vapour density of a substance? Explain this as completely as you can. *(Prel. Sc.)*

17. Deduce from first principles the relationship between molecular weight and depression of freezing-point. Assuming that the freezing-point of pure benzene is 5·493° C., and that of benzene saturated with water is 5·393° C., and also that the molecular depression in benzene is 5·1,* calculate the solubility of water in benzene at its freezing-point. *(Phar. Chem. Qual.)*

18. What is meant by the osmotic pressure of a solution, and how is it measured?

State the laws of osmotic pressure for dilute solutions.

A solution contains 50 gm. of glycerol $(C_3H_8O_3)$ per litre. Calculate its osmotic pressure in centimetres of mercury at 17° C.

($C = 12$, $H = 1$, $O = 16$. 1 atmos. = 76 cm. Hg. Molar volume of gas at S.T.P. = 22·4 litres.) *(Higher School Cert.)*

19. Explain the statement that the osmotic pressure of a certain solution is H cm. of mercury. Describe two experiments which illustrate osmosis, and state the laws of osmotic pressure.

An aqueous solution which contains 1 gm. molecule of the solute AB in 10 litres has an osmotic pressure of 300 cm. at 0° C. What conclusion can be drawn as to the state of the substance in solution? Calculate the approximate freezing-point of the solution. *(Oxford Higher School Cert.)*

* See footnote, p. 14.

20. Describe Dumas' method for the determination of vapour density. Calculate the molecular weight of a substance from the following results obtained in an experiment by this method:

Weight of bulb full of air = 25·458 gm.

Weight of bulb full of vapour = 25·965 gm.

Temperature of bath 518° C. Temperature of room 15° C.

Barometric pressure 743 mm. Capacity of bulb 224 c.c.

Density of air 1·29 gm. per litre.

(Changes in the volume of the bulb due to alterations of temperature may be neglected.)   (*Cambridge Higher School Cert.*)

21. Describe in some detail how you would determine the molecular weight of a volatile compound by Victor Meyer's method.

In an experiment of this kind the following results were obtained:

Wt. of substance	..	..	..	.. 0·062 gm.
Vol. of air ..	..	..	..	.. 23·2 c.c.
Temp. of room	..	..	..	.. 20° C.
Barometer ..	..	..	..	.. 740 mm.

Calculate the molecular weight of the compound.

(*Cambridge Higher School Cert.*)

22. Describe V. Meyer's method of determining the vapour density of a volatile substance.

Calculate the molecular weight of a substance from the following results obtained by this method. Weight of substance taken = 0·224 gm. Volume of air displaced = 46 c.c. Temperature of room 20° C. Pressure 755 mm. Pressure of aqueous vapour at 20° C. 17·4 mm.   (*Cambridge Higher School Cert.*)

23. Describe in some detail how you would find the molecular weight of a substance in solution by determining accurately the lowering of the freezing point of the solvent. In an experiment of this kind a solution of 1·9 gm. of a substance in 128 gm. of water froze at —0·36° C. Calculate the molecular weight of this substance (K = 18·6° C. per 100 gm. of water).

(*Cambridge Higher School Cert.*)

24. Describe two methods by which the molecular weights of chemical compounds may be determined, illustrating your answer by reference to the determinations of the molecular weights of two of the following: sulphur dioxide, chloroform, glucose (each description should be limited to a sketch of the apparatus and about half a page of writing).

A solution of cane sugar is in equilibrium with ice at $-2°$ C. Calculate the osmotic pressure of the solution at this temperature. (Cryoscopic constant for 100 gm. of water $= 18.6$.)

(*Cambridge Higher School Cert.*)

25. Describe a method by which you could determine the molecular weight of (*a*) an easily volatilized substance, (*b*) a non-volatile substance soluble in benzene.

(*I. M. B., London.*)

CHAPTER II

The Hydrocarbons

The Nature of the Carbon Atom.

1. The carbon atom is tetravalent, and may be represented as follows:

$$-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-$$

The straight lines indicate the four valencies of the carbon atom, but they must not be regarded as anything material; in all probability whatever physical significance they have is electrical.

2. The four valencies of carbon are all equal, since a mono-substituted derivative of methane, for instance, exists in one form only:

$$H-\overset{\displaystyle \overset{H}{|}}{\underset{\displaystyle \underset{H}{|}}{C}}-H \qquad H-\overset{\displaystyle \overset{H}{|}}{\underset{\displaystyle \underset{H}{|}}{C}}-Cl \qquad H-\overset{\displaystyle \overset{H}{|}}{\underset{\displaystyle \underset{H}{|}}{C}}-OH$$

Methane   Methyl chloride   Methyl alcohol
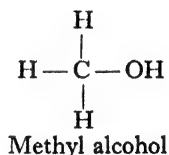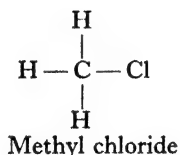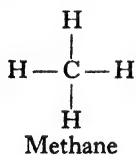
3. The carbon atom and its compounds may be represented by structural formulæ like those above. Here the atoms are represented as lying in one plane (two dimensions), whereas in order to understand the molecule they must be regarded as being arranged in space of three dimensions (p. 254).

4. The atoms or groups held together by the four valencies

of the carbon atom cannot readily exchange places with each other. (Le Bel—van't Hoff Law, 1874.)

5. Carbon atoms can be connected together by either one, two, or three valencies. The straight lines joining these atoms are known as " bonds " or " linkages ":

$$C — C \qquad C = C \qquad C \equiv C$$
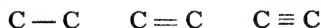
6. A number of carbon atoms may unite together, forming what are known as " carbon chains ":

$$C — C — C — C \qquad C — C = C — C \qquad C — C \equiv C — C$$

7. Carbon atoms may form either **Open Chains** or **Closed Chains.** Open Chains have separate carbon atoms at each end, as in 6. Closed or Ring-shaped Chains have the first and last carbon atom linked together, and may be represented as
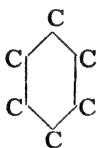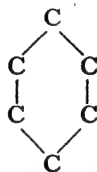
8. The atoms of polyvalent elements may take part in the formation of both open and closed chains.
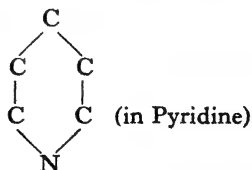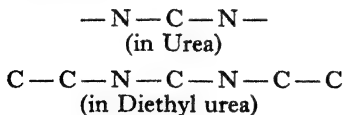
9. The number of carbon atoms in the organic molecule may be large.

Classification of Organic Compounds.

Organic Compounds are, broadly speaking, divided into two main classes:

(*a*) <u>Aliphatic Compounds.</u>
(*b*) <u>Aromatic Compounds.</u>

The term **aliphatic** is derived from the Greek word ἀλειφαρ (*aleiphar*), fat, since the most important members are found among the fats. The aliphatic compounds are sometimes regarded as derivatives of marsh gas, which is the simplest representative member of the series.

The aliphatic compounds are, as a rule, open-chain compounds.

The term **aromatic** was originally given to those compounds which could not be classed with the aliphatic series of compounds. They are often distinguished from the latter by possessing an aromatic smell, e.g. oil of cloves, turpentine, balsams, natural resins.

The aromatic compounds are closed-chain or ring-compounds (Kekulé). They will be discussed later.

Organic compounds can also be classified into well-defined groups, e.g. Paraffins, Fatty acids, Aldehydes, Ketones; each group is composed of a series of compounds which consist of the same elements but whose molecular weights increase by a fixed amount (usually 14). Such a series is known as a homologous series.

A Homologous Series may be defined as a family of chemically related compounds, the composition of which varies (Gerhardt), or, a Homologous Series is formed when compounds with similar chemical structure and similar chemical properties are grouped together and arranged in order of their molecular complexity.

Two such series are appended.

The Paraffins		*The Fatty Acids*	
CH_4		H COOH	
C_2H_6	Difference	CH_3COOH	Difference
C_3H_8	CH_2	C_2H_5COOH	CH_2
C_4H_{10}, &c.		C_3H_7COOH, &c.	

In any such homologous series a number of generalizations can be made:

1. A general formula can be written down for each homologous series which represents the composition of all the members of the series.

Paraffins: C_nH_{2n+2} Fatty Acids: $C_nH_{2n}O_2$ or
$$C_nH_{2n+1} \cdot COOH$$

2. The physical properties, such as the melting-point, boiling-point, specific gravity and solubility, show a well-marked gradation. In general it may be said that the melting-point (m. pt.) and boiling-point (b. pt.) rise from the lower to the higher members of the series.

3. The chemical properties differ very little. Hence the chemical reactions of one apply to other members of the same series.

The Hydrocarbons

The Hydrocarbons consist of a number of compounds which contain two elements only, namely, carbon and hydrogen. These hydrocarbons can be subdivided into a number of homologous series, namely,

(A) The Paraffins or Methane series, which are saturated hydrocarbons (p. 59).

(B) The Olefines or Ethylene series, which are unsaturated hydrocarbons (p. 59).

(C) The Acetylenes, which are unsaturated hydrocarbons.

The Saturated Hydrocarbons (Paraffins)

The Paraffins have the general formula

$$C_nH_{2n+2}$$

and comprise

Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Pentane	C_5H_{12}, &c.

Methane, Marsh Gas, CH_4.

Occurrence.—In stagnant water. In gas wells at Baku, Pittsburg, &c. As " fire-damp " in coal mines. Coal gas contains as much as 40 per cent of methane. In the case of stagnant water containing vegetable matter the cellulose present in this matter is hydrolysed as follows:

$$(C_6H_{10}O_5)_n + nH_2O = 3nCO_2 + 3nCH_4$$
Cellulose
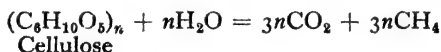
Formation.

1. By the direct union of carbon and hydrogen at 1200° C

2. By passing a mixture of hydrogen sulphide and carbon disulphide over red-hot copper:

$$2H_2S + CS_2 + 8Cu = 4Cu_2S + CH_4$$
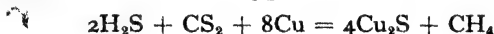
3. By heating anhydrous sodium acetate or potassium acetate with soda lime:

$$CH_3|COO\ Na = CH_4 + Na_2CO_3$$
$$|\ +$$
$$H\ |ONa$$
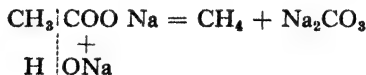
Experiment.—To prepare methane and to examine its properties.

Procedure.—Fit up the apparatus shown in fig. 13. Mix intimately in a mortar 4 gm. of either anhydrous sodium acetate or potassium acetate and 16 gm. of soda-lime. Transfer this mixture to the hard glass test tube and heat
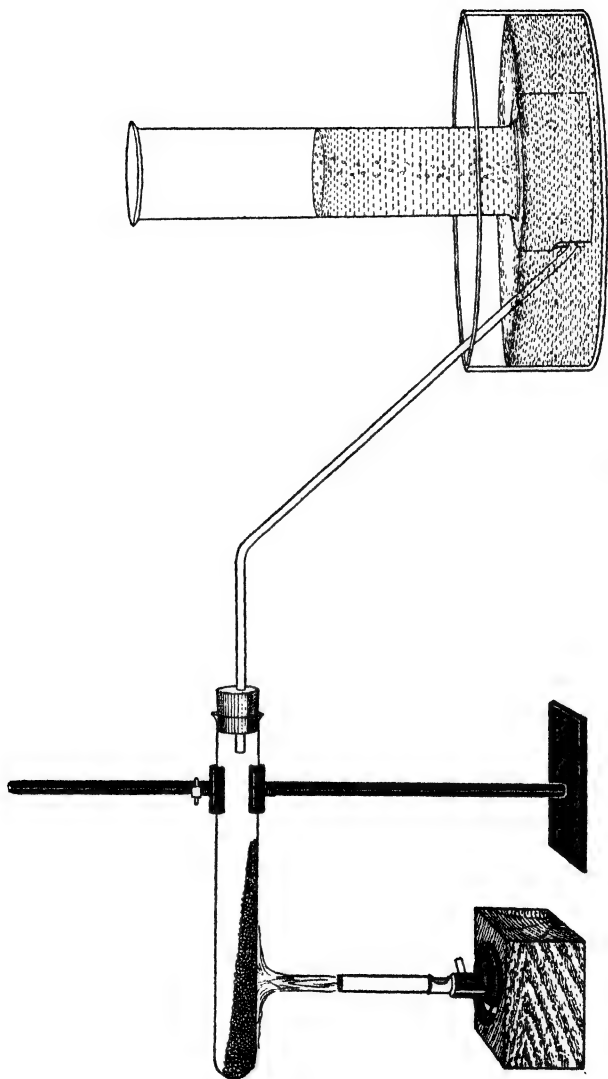
Fig. 13.—Preparation of Methane

gently at first. When the air has been expelled from the apparatus (indicated by the absence of an explosion when a light is applied to a test tube of the gas) collect several jars of the gas and apply the following tests:

(*a*) Note the colour and odour of the gas.

(*b*) Apply a lighted taper and push the taper into the gas jar; note that the gas burns but the taper is extinguished.

(*c*) Add lime water to the gas jar immediately after the gas has burned; turbidity is produced, owing to the formation of carbon dioxide.

(*d*) Add lime water to the unburnt gas: no turbidity results.

(*e*) Shake a test tube full of the gas with caustic soda solution in a beaker: no absorption takes place.

(*f*) Add bromine water: no result.

(*g*) Add potassium permanganate solution: no result.

4. By decomposing zinc methyl with water:

$$Zn(CH_3)_2 + 2H_2O = 2CH_4 + Zn(OH)_2$$

5. By dropping a mixture of methyl iodide and methyl alcohol on to a zinc-copper couple:

$$CH_3 \overline{| I + Zn + CH_3O |} H = Zn \cdot I \cdot OCH_3 + CH_4$$

Methyl	Methyl	Zinc
iodide	alcohol	methoxyiodide
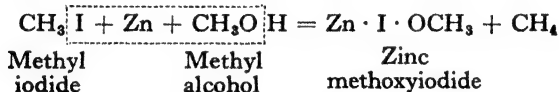
6. Methane is also prepared in the laboratory by adding small quantities of water or very dilute hydrochloric acid slowly by means of a separating or dropping funnel to say 15 gm. of aluminium carbide contained in a flask fitted with a delivery tube (cf. fig. 17, p. 78).

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$$

Properties.—Colourless gas, no smell. Condenses to a liquid at 11° C. under a pressure of 180 atmospheres. B. pt. —164° C.; m. pt. —186° C.; sp. gr. 0·554 at 0° C. Burns

in the air with a pale blue non-luminous flame and forms a highly explosive mixture when mixed with air or oxygen:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
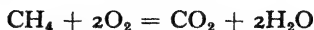
The gas is almost insoluble in water, but more soluble in alcohol. It is very stable towards oxidizing agents and is not attacked, or only very slightly so, by nitric acid, chromic acid, potassium permanganate, concentrated sulphuric acid, and strong alkalis. This stability towards oxidizing agents and other compounds is a general characteristic of saturated compounds like the paraffins.

Chlorine and bromine, however, react with methane as follows:

$$\begin{array}{ccc} H & & H \\ | & & | \\ H-C-H + Cl_2 & = & H-C-Cl + HCl \\ | & & | \\ H & & H \end{array}$$
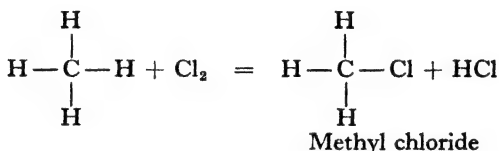
$$\text{Methyl chloride}$$

Bromine acts similarly, giving methyl bromide.

The replacement of hydrogen by chlorine can take place in stages; the process is termed *substitution* and the products *substitution products*. Methyl chloride in the above equation is a substituted product of methane.

A Saturated Compound is one in which the maximum capacity of all the carbon atoms is exerted, and which can yield derivatives only by substitution.

An Unsaturated Compound is one which is capable of forming additive compounds.

Ethane, C_2H_6.

Formation.

1. By the action of zinc or sodium on methyl iodide:

$$2CH_3I + Zn = CH_3 \cdot CH_3 + ZnI_2$$

2. By reducing ethyl iodide with zinc-copper couple:

$$C_2H_5I + 2H = C_2H_6 + HI$$
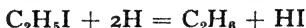
3. By decomposing zinc ethyl with water:

$$Zn(C_2H_5)_2 + 2H_2O = 2C_2H_6 + Zn(OH)_2$$
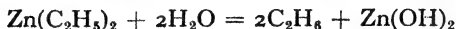
4. By treating ethylene with nascent hydrogen:

$$C_2H_4 + 2H = C_2H_6$$
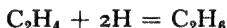
5. By treating methyl iodide with zinc methyl:

$$2CH_3I + Zn(CH_3)_2 = 2C_2H_6 + ZnI_2$$
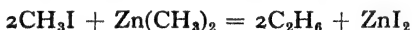
6. By electrolysing a dilute solution of acetic acid or a concentrated solution of potassium acetate:

$$\begin{array}{ccc} CH_3 \vert COO \vert H & & CH_3 \\ + & = & \vert \quad + 2CO_2 + H_2 \\ CH_3 \vert COO \vert H & & CH_3 \end{array}$$

Acetic acid   Ethane
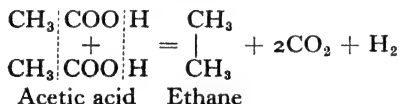
Properties.—Colourless gas, condensing at 4° C. under a pressure of 46 atmospheres. Slightly soluble in water and alcohol, more so than methane. Burns in air with a feebly luminous flame. Very stable towards oxidizing agents, e.g. HNO_3, CrO_3, and towards alkalis and concentrated sulphuric acid. It gives substitution products with chlorine and bromine.

Constitution of the Paraffins.

The reaction between zinc and methyl iodide affords strong evidence in support of Kekulé's *Theory of the Linking of Carbon Atoms*, which states that

" Carbon atoms can not only attach themselves to other elements by their bonds but are capable of being linked to one another."

The reaction mentioned can be expressed by the following constitutional formula:

$$
\begin{array}{ccccc}
\text{H} & & \text{H} & & \text{H} \quad \text{H} \\
| & & | & & | \quad\; | \\
\text{H}-\text{C}-\boxed{\text{I}+\text{Zn}+\text{I}}-\text{C}-\text{H} & = & \text{H}-\text{C}-\text{C}-\text{H}+\text{ZnI}_2 \\
| & & | & & | \quad\; | \\
\text{H} & & \text{H} & & \text{H} \quad \text{H}
\end{array}
$$
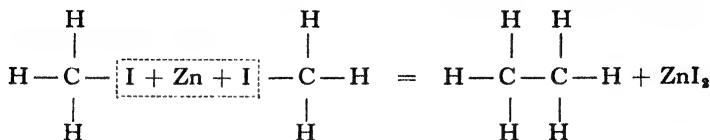
It is abundantly clear, since zinc iodide is formed, that the two methyl groups (CH_3—) left unite by means of their carbon atoms to form ethane; this can be the only linking which will render the carbon atom tetravalent and the hydrogen monovalent. (It should be noted that ethane is also called dimethyl.)

The paraffins give rise to what are known as **Alkyl** radicles. Methane gives the name to the radicle methyl CH_3—, ethane to ethyl C_2H_5—, propane to propyl C_3H_5—, butane to butyl C_4H_9—, &c. These radicles are monovalent. Commencing with methane, it is possible to build up the paraffin series of compounds theoretically by substituting a methyl group for a hydrogen atom.

$$
\begin{array}{cc}
\begin{array}{c}
\text{H} \\
| \\
\text{H}-\text{C}-\text{H} \\
| \\
\text{H} \\
\text{Methane}
\end{array}
\quad \text{gives} \quad
\begin{array}{c}
\text{H} \quad \text{H} \\
| \quad\; | \\
\text{H}-\text{C}-\text{C}-\text{H} \\
| \quad\; | \\
\text{H} \quad \text{H} \\
\text{Ethane}
\end{array}
\end{array}
$$

$$
\begin{array}{cc}
\begin{array}{c}
\text{H} \quad \text{H} \\
| \quad\; | \\
\text{H}-\text{C}-\text{C}-\text{H} \\
| \quad\; | \\
\text{H} \quad \text{H} \\
\text{Ethane}
\end{array}
\quad \text{gives} \quad
\begin{array}{c}
\text{H} \quad \text{H} \quad \text{H} \\
| \quad\; | \quad\; | \\
\text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\
| \quad\; | \quad\; | \\
\text{H} \quad \text{H} \quad \text{H} \\
\text{Propane}
\end{array}
\end{array}
$$
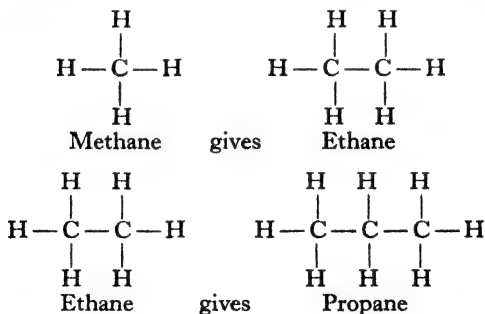
In the case of propane, however, the hydrogen atoms are not attached to all the carbon atoms in the same manner. Two carbon atoms have three attached hydrogen atoms but one carbon atom has only two hydrogen atoms linked to it.

Hence when a methyl group is inserted it is possible to obtain two different compounds from it, namely, normal butane and isobutane, thus:

$$
\begin{array}{ccccc}
& \text{H} & \text{H} & \text{H} & \\
& | & | & | & \\
\text{H}- & \text{C}- & \text{C}- & \text{C}- & \text{H} \\
& | & | & | & \\
& \text{H} & \text{H} & \text{H} &
\end{array}
\;\rightarrow\;
\begin{array}{ccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \\
| & | & | & | & \\
\text{H}-\text{C}- & \text{C}- & \text{C}- & \text{C}- & \text{H} \\
| & | & | & | & \\
\text{H} & \text{H} & \text{H} & \text{H} &
\end{array}
$$

Propane   Normal butane

and

$$
\begin{array}{ccc}
\text{H} & \text{H} & \text{H} \\
| & | & | \\
\text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\
| & | & | \\
\text{H} & & \text{H} \\
& \text{H}-\text{C}-\text{H} \\
& | \\
& \text{H}
\end{array}
$$

Isobutane
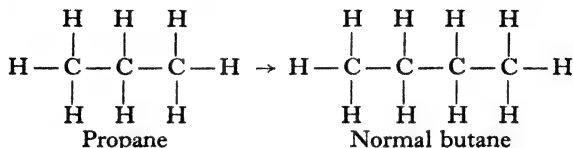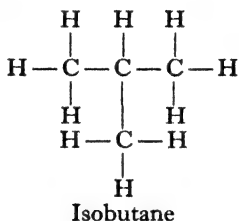
These two compounds have the same molecular formula but different constitutions. One is said to be the **isomeride** of the other, or to be **isomeric** with the other, and the phenomenon is known as **isomerism**.

Again, it is possible to obtain three compounds of the same molecular formula from the butanes by substituting a CH_3- group for a hydrogen atom:

$$
\begin{array}{ccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
| & | & | & | & | \\
\text{H}-\text{C}- & \text{C}- & \text{C}- & \text{C}- & \text{C}-\text{H} \\
| & | & | & | & | \\
\text{H} & \text{H} & \text{H} & \text{H} & \text{H}
\end{array}
$$

Normal Pentane, b. pt. 36° C.
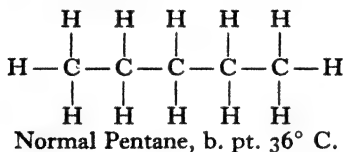
The Normal Paraffin contains a primary group, consisting of a carbon atom united to 2 other carbon atoms and 2 hydrogen atoms.

$$
\begin{array}{c}
\text{H} \\
| \\
-\text{C}-\text{C}-\text{C}- \\
| \\
\text{H}
\end{array}
$$

Primary group

$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H-C-C-C-C-H \\ | \quad | \quad | \quad | \\ H \quad H \quad H \quad H \end{array}$$
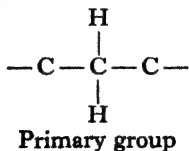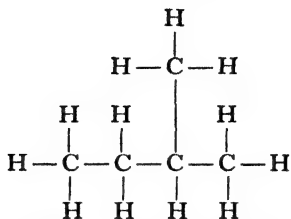
Isopentane, b. pt. 28° C.

The Iso Paraffin contains a secondary group, consisting of a carbon atom united to 3 other carbon atoms and 1 hydrogen atom.

$$\begin{array}{c} H \\ | \\ -C-C-C- \\ | \\ -C- \end{array}$$

Secondary group

$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H-C-C-C-H \\ | \quad | \quad | \\ H \quad | \quad H \\ H-C-H \\ | \\ H \end{array}$$
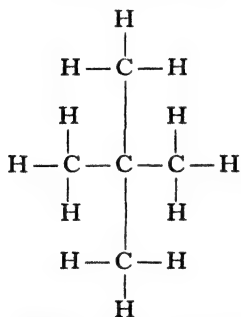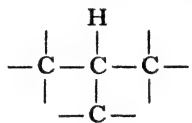
Neopentane, b. pt. 9° C.

The Neo Paraffin contains a tertiary group, consisting of a carbon atom united to 4 other carbon atoms only.

$$\begin{array}{c} -C- \\ | \\ -C-C-C- \\ | \\ -C- \end{array}$$

Tertiary group
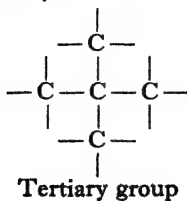
An **Isomeric Compound is one which has the same molecular formula as another compound but differs from it in constitution and in both physical and chemical properties.**

Propane, C_3H_8, occurs in petroleum.

Formation.

1. By heating a mixture of ethyl and methyl iodides with sodium:
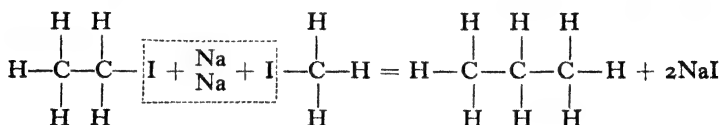
This reaction is employed in the determination of the constitution of propane.

2. By reducing propyl iodide or isopropyl iodide with the zinc-copper couple and water:

$$C_3H_7I + 2H = C_3H_8 + HI$$
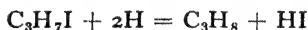
Properties.—A gas, which burns with a more luminous flame than ethane. It reacts with chlorine in diffused sunlight to form propyl chloride:

$$C_3H_8 + Cl_2 = C_3H_7Cl + HCl$$
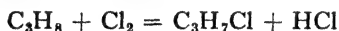
Butanes, C_4H_{10}.

Normal Butane occurs in petroleum and is formed by heating ethyl iodide with sodium:
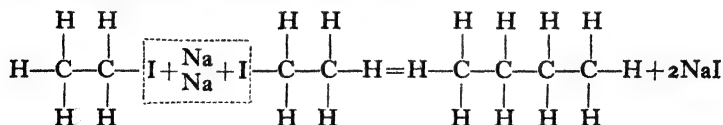
This reaction is employed in the determination of the constitution of normal butane.

Properties.—A gas which liquefies at about 0° C. It gives substitution products with chlorine.

Isobutane, Trimethylmethane, is formed when tertiary butyl iodide is reduced with nascent hydrogen:

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - I + 2H = CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - H + HI$$
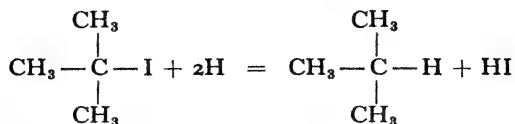
Properties.—A gas which liquefies at $-17°$ C. It also forms substitution products with chlorine.

Pentanes, C_5H_{12}.

Normal pentane and **Isopentane** are colourless liquids which occur in petroleum.

Neopentane is obtained synthetically by the action of tertiary butyl iodide on zinc methyl:

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \boxed{I + Zn + I} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 = 2CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 + ZnI_2$$
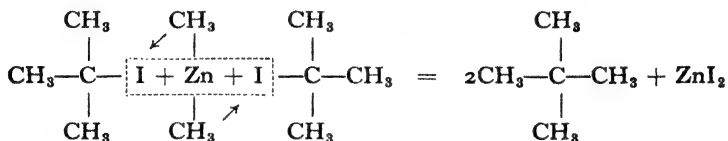
Properties.—A gas at ordinary temperatures, which condenses to a colourless liquid at $9°$ C.

Petroleum

Crude petroleum is found in Nature and is in all probability a product of the decomposition of vegetable and animal remains. It occurs mainly in porous sandstone in " pockets " roofed over by impervious rock, such as clay or shale. The oil is obtained from these wells by drilling, and when the oil pocket is pierced, the gas pressure sometimes forces the oil out as a " gusher "; more frequently air pressure has to be applied in order to force the oil out

of the well. In either case the oil is controlled and conveyed away by a system of pipe-lines to a refinery.

Crude petroleum oil varies in colour from pale yellow to black; some kinds are very mobile, others viscous. The composition varies greatly. The specific gravity varies from under 0·8 to over 1·0.

Petroleum is composed principally of saturated hydrocarbons and the products vary according to its location.

American Petroleum consists of saturated paraffins, C_nH_{2n+2}. The first paraffin, methane, is found in natural gas. Pentane and hexane are found in commercial benzine. (Benzine must not be confused with the aromatic hydrocarbon benzene, C_6H_6 (see p. 387)). The paraffins $C_{13}H_{28}$ and $C_{18}H_{38}$ are found in light petroleum.

Russian Petroleum (Baku) contains a number of hydrocarbons of the naphthene series, C_nH_{2n}, such as heptanaphthene C_7H_{14}, $C_{15}H_{30}$. These, also called cyclic polymethylenes, differ from unsaturated olefines of the same formula, since they do not react with bromine, nitric acid and sulphuric acid.

Crude petroleum is usually treated with sulphuric acid followed by a wash with caustic soda, and is then subjected to fractional distillation. The fractions collected are usually treated in a similar manner. The increased demand for motor spirit has led to the " cracking process ", by which oils of high boiling point are converted to motor spirit of low boiling point in a cracking still. For example, the paraffin $C_{13}H_{28}$ may be " cracked " to yield pentane and an unsaturated hydrocarbon, the cracking taking place at the dotted line shown:

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \,|\, CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$$

The pentane formed ($CH_3CH_2CH_2CH_2CH_3$) must have taken an atom of hydrogen from the right-hand portion, leaving an unsaturated $CH_3-(CH_2)_6-CH=$ group.

Cracking of the same substance may also take place at other parts of the molecule, yielding other paraffins. Similarly for other higher hydrocarbons.

On distillation from a fractionating column still, the following fractions are obtained.

PETROLEUM OIL PRODUCTS

Fraction and Percentage	Distillate	Specific Gravity	Temperature

I. 15·5–16·5%	**Benzine. Petroleum Naphtha. Petroleum Spirit.**
	 (*a*) Petroleum ether or Petrol.
	 (*b*) Benzine.*
	   1. Benzoline or Gasoline or Petrol.
	   2. Naphtha.
	 (*c*) Ligroin or Light Petroleum.
	 (*d*) Polishing oil.
		
		0·64–0·65
		0·70–0·72
		
		0·73
		0·74–0·77
			under 150° C.
			
			40–70°
			70–120°
			
			70–90°
			90–120°
			
			120–135°
			130–160°

II. 50–55%	**Kerosene (Paraffin Oil).** Gas oil.	0·802	150–300° C.
III. 10–25%	**Lubricating (A) Oils, (B) Greases.** Vaseline or Petroleum jelly.	0·875	300–400° C.
IV. 2%	**Paraffin Wax.**		above 400° C.
V. 8–10%	**Coke. Asphalt.** (Ozokerite).		Residue

* Not to be confused with coal-tar *benzene*, p. 387.

Uses of Petroleum products.

Petroleum ether, for cleansing purposes and as a solvent in organic extractions.

Petrol, as a motor fuel, and as a solvent for extracting oil from beans and seeds, e.g. linseed oil, and greases from bones, e.g. bone oil. As a solvent for rubber in the manufacture of rubber solutions. In the removal of oils and greases by dyers and cleaners and as a thinner in cellulose lacquers.

Ligroin, for dyers' and cleaners' purposes and for metal polishes.

Kerosene, for illuminating purposes and as a fuel for heating purposes in oil stoves.

Gas Oil, for Diesel engines and for enriching coal gas.

Lubricating oil, used either alone or mixed with fatty oils for lubrication (Castrol X.L.). When highly refined, for medicinal purposes, and when blended with metallic soaps, for greases.

Vaseline or *Petroleum jelly*, for creams and ointments.

Paraffin wax for candles, boot and furniture polishes, gramophone records, and waxed paper.

Asphalt, for roads, under the name of bitumen; also for roofing felt.

Ozokerite is a naturally occurring solid paraffin also known as Earth wax, found in Rumania and in the island of Cheleken in the Caspian Sea. It is the solid residue left behind when petroleum evaporates. When refined it is put on the market under the name *Ceresine* and is used for candles, for making furniture and shoe polishes, and for preparing insulating compounds in electrical work.

The Unsaturated Hydrocarbons

There are two important families of unsaturated hydro-carbons: (*a*) the Olefines, (*b*) the Acetylenes,

The Olefines

The Olefines form a homologous series of the general formula

$$C_nH_{2n},$$

e.g.   Ethylene C_2H_4
Propylene C_3H_6

A hydrocarbon of this series contains two atoms of hydrogen less than the corresponding paraffin hydrocarbon with the same number of carbon atoms. The first member of the series is ethylene, formerly called olefiant (oil-forming) gas.

Ethylene, Olefiant Gas, C_2H_4.

Occurrence.—In the destructive distillation of complicated organic compounds, and in the distillation of higher paraffins. Illuminating gas consequently contains the olefines C_2H_4, C_3H_6, C_4H_8 to the extent of 4 to 5 per cent.

Formation.

1. By reducing acetylene (in the form of copper acetylide) with zinc dust and ammonia:

$$C_2H_2 + 2H = C_2H_4$$
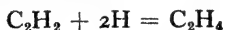
2. By dehydrating ethyl alcohol (by heating with concentrated sulphuric acid or by dropping the alcohol on to phosphorus pentoxide or anhydrous zinc chloride mixed with sand and heated to 220° C.):

$$C_2H_5OH - HOH = C_2H_4$$

Experiment.—To prepare ethylene and to examine its properties.

Procedure.—Fit up the apparatus shown in fig. 14. Put 25 gm. of phosphorus pentoxide in the 300 c.c. round-bottomed flask; as the pentoxide is very deliquescent, this must be done rapidly. Heat the flask gently on a sand tray
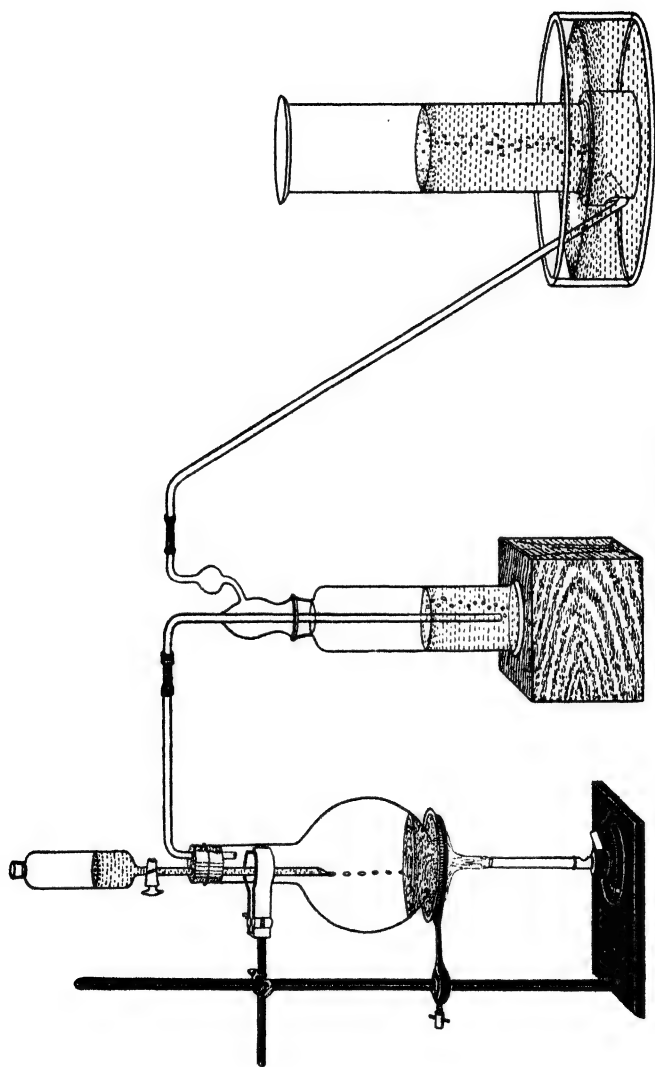
Fig. 14.—Preparation of Ethylene

and add alcohol slowly from the separating funnel. The gases evolved, which consist of ethylene, alcohol vapour, and ether, are passed through concentrated sulphuric acid contained in a wash-bottle, in order to absorb the alcohol and ether. Before the ethylene is collected in gas jars, a test tube of the gas is collected and a light applied. When all the air has been expelled from the apparatus the gas will burn without explosion. Now collect a number of jars of the gas and carry out the following tests:

(*a*) Note colour and odour.

(*b*) Apply a lighted taper. Note that the gas burns with a smoky luminous flame, but does not support combustion, as is shown by plunging the taper into the centre of the gas jar.

(*c*) Burn the gas, add lime water, and shake well: turbidity is produced.

(*d*) Shake up the unburnt gas with lime water: no turbidity.

(*e*) Add a little bromine water: the bromine is slowly absorbed and decolorized.

(*f*) Add a little potassium permanganate solution and shake well: the colour is discharged.

(*g*) Add caustic soda solution and shake: no reaction.

3. By dropping ethyl bromide on to boiling alcoholic potash:

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O$$

4. By heating methylene iodide with copper at 100° in a sealed tube:

$$2CH_2I_2 + 4Cu = C_2H_4 + 2Cu_2I_2$$

5. By electrolysis of potassium succinate:

$$\begin{array}{l} CH_2 \vdots COO \vdots K \\ | \\ CH_2 \vdots COO \vdots K \end{array} = \begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + 2CO_2 + 2K$$
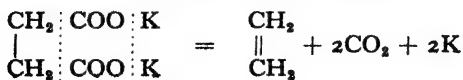
Properties.—Colourless gas with a sweetish taste and smell. It liquefies at 10° C. under a pressure of 10 atmospheres. It is sparingly soluble in water. It burns with a luminous flame and forms a highly explosive mixture with air or oxygen.

The chemical properties of the olefines differ materially from those of the paraffins. Most of the special chemical characteristics are due, no doubt, to the double bond, e.g. $CH_2 = CH_2$. Ethylene is taken to illustrate these properties.

Reactions of the Olefines.

1. They burn with a luminous smoky flame.

2. They form saturated additive compounds with H_2, Br_2, Cl_2, HI, concentrated H_2SO_4, &c., but not with HCl:

$$(a) \quad \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + 2H = \underset{\text{Ethane}}{C_2H_6}$$

$$(b) \quad \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \begin{matrix} Cl \\ | \\ Cl \end{matrix} = \begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}$$
$$\text{Ethylene chloride}$$

$$(c) \quad \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + HI = \begin{matrix} CH_3 \\ | \\ CH_2I \end{matrix}$$
$$\text{Ethyl iodide}$$

$$(d) \quad \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + SO_2 \begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} = \begin{matrix} CH_3 \\ | \\ CH_2 \cdot O \cdot SO_2 . OH \end{matrix}$$
$$\text{Ethyl hydrogen}$$
$$\text{sulphate}$$
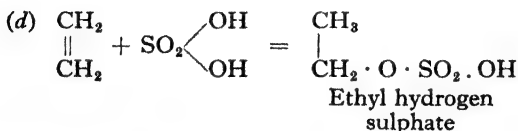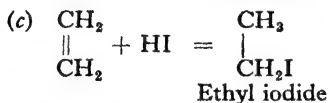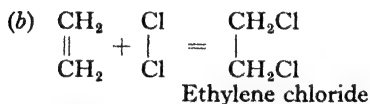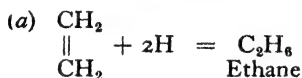
3. Hypochlorous acid (HOCl) can also form additive products, converting the olefines into **chlorhydrins:**

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + HOCl = \begin{matrix} CH_2Cl \\ | \\ CH_2OH \end{matrix}$$
$$\text{Ethylene chlorhydrin}$$
$$\text{(Glycol chlorhydrin)}$$
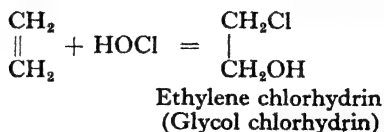
4. They differ from the paraffins in being readily oxidized by potassium permanganate or chromic acid (but not by cold nitric acid):

$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + O + HOH = \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

Ethylene glycol
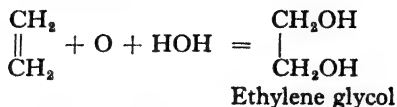
Constitution of the Olefines.

Ethylene may have the following formulæ:

$$\begin{array}{ccc} \mathrm{I} & \mathrm{II} & \mathrm{III} \\ CH_3 & CH_2- & CH_2 \\ | & | & \| \\ CH= & CH_2- & CH_2 \end{array}$$
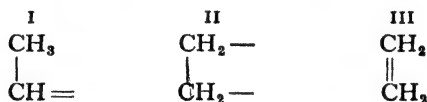
In formulæ I and II two free carbon bonds or valencies are assumed in the ethylene molecule. In formula III the free bonds are used in linking the carbon atoms.

Ethylene is formed when ethyl bromide is heated with alcoholic potash, which takes away one atom each of hydrogen and bromine.

The constitution of ethyl bromide is:

$$\begin{array}{ccc} & H & H \\ & | & | \\ H - & C - & C - Br \\ & | & | \\ & H & H \\ & (b) & (a) \end{array}$$
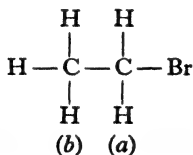
and the hydrogen atom may be taken either from position (a) or position (b), giving the following formulæ for ethylene:

$$\begin{array}{ccccc} \mathrm{I} & & \mathrm{II} & & \mathrm{III} \\ H \quad H & & H \quad H & & H \quad H \\ | \quad | & & | \quad | & & | \quad | \\ H-C-C- & \text{or} & H-C-C-H & \text{or} & H-C=C-H \\ | & & | \quad | & & \\ H & & & & \end{array}$$
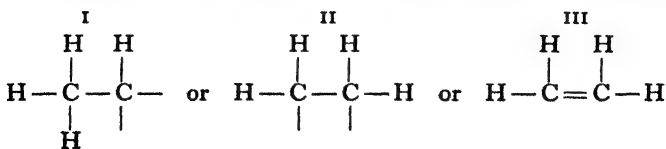
If ethylene has the constitution I, ethylene dibromide, formed by direct combination of ethylene with bromine, should be represented as follows:

$$\begin{array}{ccc} & H & H \\ & | & | \\ H - & C - & C - Br \\ & | & | \\ & H & Br \end{array}$$
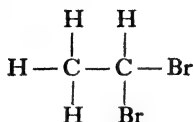
But the compound $CH_3 \cdot CHBr_2$, known as ethylidene dibromide, is prepared in another way and has different properties, so it cannot have the same constitution. Hence ethylene dibromide must be represented as follows:

$$\begin{array}{ccc} & H & H \\ & | & | \\ H - & C - & C - H \\ & | & | \\ & Br & Br \end{array}$$
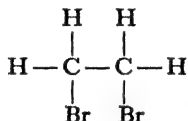
Thus the constitution should be represented by formula II; but in this formula the four valencies of the carbon atom are not used up; hence formula III is taken as correct, illustrating the linking by double bonds.

Again, each of the formulæ I and II would give rise to a different bromine derivative, whereas only one can be formed if formula III is accepted, and, in fact, only one is known.

Reasons for the Assumption of the Double Bond.

1. It is impossible to prepare hydrocarbons such as

$$\begin{array}{ccc} H & H & \\ | & | & | \\ H - C - & - C - & \text{or} & - C - H \\ | & | & | \\ H & H & \end{array}$$
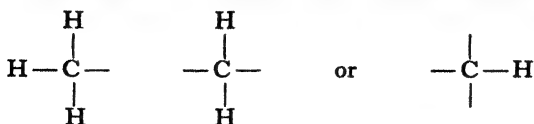
2. The carbon atom is in an "unsatisfied" condition; hence the compound is unsaturated and is capable of

uniting readily with two monovalent atoms or radicles to form a " satisfied " or saturated compound.

3. Production of ethylene by the electrolysis of succinic acid.

4. Action of copper or zinc on methylene iodide:

$$
\begin{array}{c}
CH_2 \,\vert\, I_2 \\
\quad\quad + 4Cu \\
CH_2 \,\vert\, I_2
\end{array}
=
\begin{array}{c}
CH_2 \\
\| \\
CH_2
\end{array}
+ 2Cu_2I_2
$$
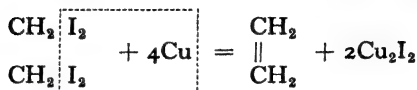
Propylene, C_3H_6.

Formation.

1. By heating propyl alcohol (4 volumes) with sulphuric acid (3 volumes) and 5 per cent of anhydrous aluminium sulphate at 105° C. This reaction is one of dehydration:

$$CH_3CH_2CH_2OH - HOH = CH_3 \cdot CH{=}CH_2$$

2. By boiling either propyl bromide or isopropyl bromide with alcoholic potash:
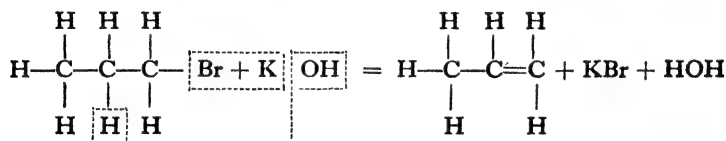
Propyl bromide
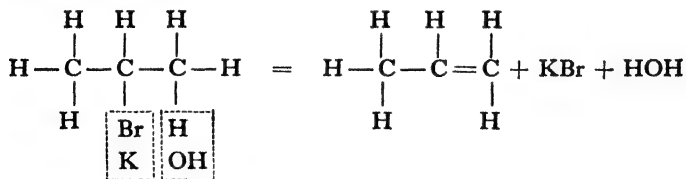
This is a case in which a bromine atom and a hydrogen atom are removed from adjacent carbon atoms.

Properties.—Colourless gas, similar in properties to

ethylene. It combines readily with bromine to form propylene dibromide, $CH_3 \cdot CHBr \cdot CH_2Br$, an oily liquid (b. pt. 141° C.); this indicates that propylene is an unsaturated compound.

The Olefines give rise to what is known as **alkylene** radicles. Ethylene gives the name to the radicle Ethylene, $C_2H_4=$, &c. These radicles are divalent.

The Acetylenes

The acetylenes also form a homologous series of the general formula:

$$C_nH_{2n-2},$$

e.g. $CH \equiv CH$ $CH_3 \cdot CH_3$
       Acetylene   from   Ethane

$CH_3 \cdot C \equiv CH$ $CH_3 \cdot CH_2 \cdot CH_3$
   Allylene or   from   Propane
   Propine
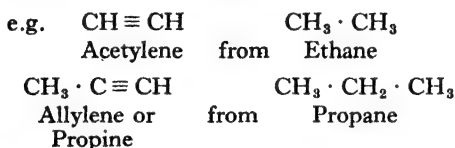
A hydrocarbon of this series contains four hydrogen atoms less than the corresponding paraffin hydrocarbon with the same number of carbon atoms.
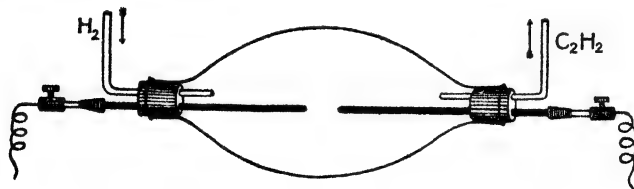
Fig. 15.—Preparation of Acetylene (Berthelot, 1859)

Acetylene, $CH \equiv\!\equiv CH.$

Occurrence.—In the dry distillation of complex compounds such as wood, lignite and coal; thus illuminating gas contains acetylene, &c.

Formation.

1. By the direct union of hydrogen with carbon caused by striking the electric arc between carbon poles in an atmosphere of hydrogen (fig. 15):

$$2C + H_2 = C_2H_2$$
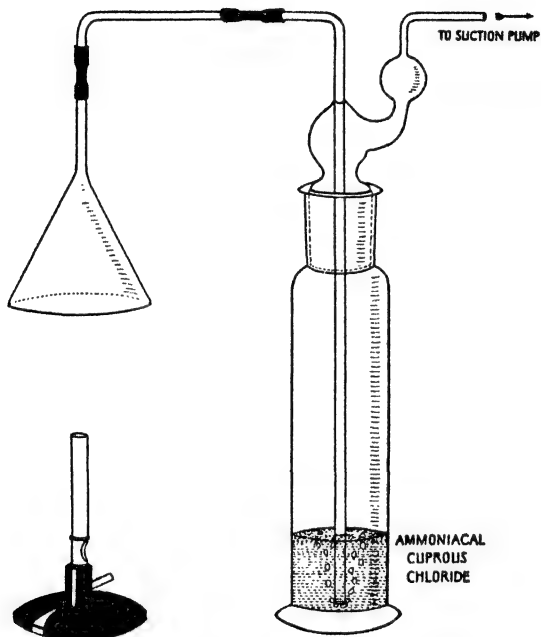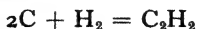
Fig. 16.—To show that acetylene is formed when a bunsen burner "strikes back"

2. By the incomplete combustion of methane, ethyl alcohol, coal gas and hydrocarbons. Acetylene is formed when the bunsen burner "strikes back" and burns within the metal tube.

Experiment.—To show that acetylene is produced when a bunsen burner burns at the bottom.

Procedure.—Fit up the apparatus shown in fig. 16. Light the gas at the base of the bunsen burner and draw the issuing gases through an ammoniacal solution of cuprous chloride contained in a Drechsel's wash-bottle, by means of a suction pump attached to the shorter tube of the bottle. The presence of acetylene in the burnt gases is indicated
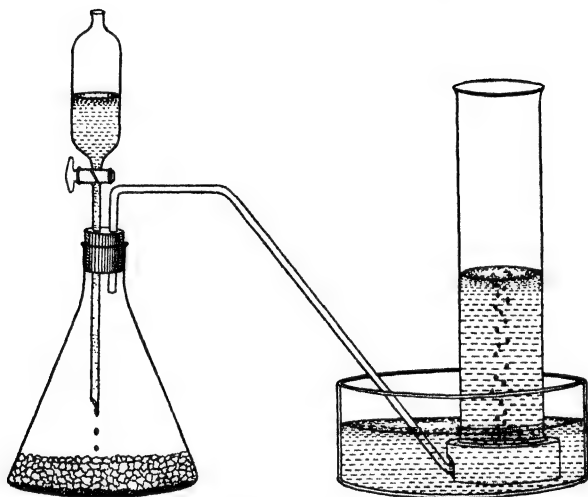
Fig. 17.—Preparation of Acetylene from Calcium Carbide

by the formation of a brown precipitate of cuprous acetylide, Cu_2C_2, in the bottle.

3. By the action of water on calcium carbide:

$$CaC_2 + 2HOH = C_2H_2 + Ca(OH)_2$$
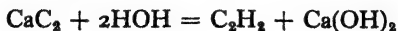
Experiment.—To prepare acetylene and to examine its properties.

Procedure.—Fit up the apparatus illustrated in fig. 17. Place a layer of sand at the bottom of the flask and then add about 30 gm. of calcium carbide. Replace the cork,

fitted with a dropping funnel and delivery tube. Allow water to drop gradually on to the carbide and make certain that all the air has been displaced from the apparatus. Then collect a few jars of the gas and apply the following tests:

(*a*) Apply a light by means of a taper: the gas does not support combustion, but burns with a very smoky flame.

(*b*) Add lime water both before and after the gas has burnt.

(*c*) Invert a jar of the gas over caustic soda solution.

(*d*) Add bromine water in small quantities: $C_2H_2Br_4$ is formed.

(*e*) Add potassium permanganate solution to another jar of gas.

Record your observations in a notebook.

4. By dropping ethylene bromide on to boiling alcoholic potash:

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + KOH \rightarrow \begin{matrix} CHBr \\ \| \\ CH_2 \end{matrix} + KOH = \begin{matrix} CH \\ \||| \\ CH \end{matrix} + KBr + H_2O$$

Ethylene bromide   Vinyl bromide   Acetylene
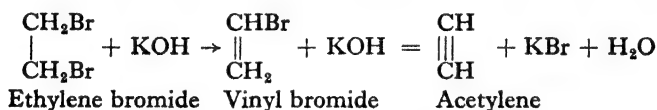
5. By the electrolysis of the potassium salt of fumaric acid:

$$\begin{matrix} CH \cdot COO\,K \\ \| \\ CH \cdot COO\,K \end{matrix} = \begin{matrix} CH \\ \||| \\ CH \end{matrix} + 2CO_2 + 2K$$

Potassium fumarate
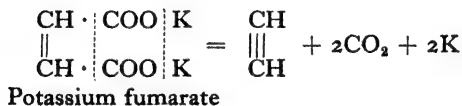
Properties.—Colourless gas, liquefies at $1°$ C. under a pressure of 48 atmospheres. The solution in acetone, when burned in oxygen, gives a flame hot enough to melt steel; hence its use in welding and cutting metal. It is somewhat soluble in water, more so in alcohol and acetone. Acetylene is a strongly endothermic compound, and hence

can be detonated. It burns with a very smoky flame rich in actinic rays (hence it is used in photography). The chemical properties are due, no doubt, to the triple bond.

Reactions.

1. It burns with a very smoky flame, with the formation of much soot.

2. It combines with:

(a) *Two* atoms of hydrogen or halogen or one molecule of halogen acid to form the *olefine* ethylene or its substitution products.

$$CH \equiv CH + 2H \quad = \quad CH_2 = CH_2$$
(by Zn and ammonia) \qquad Ethylene

$$CH \equiv CH + HBr \quad = \quad CH_2 = CHBr$$
Vinyl bromide,
or Monobromethylene

$$CH \equiv CH + Br_2 \quad = \quad CHBr = CHBr$$
Acetylene dibromide
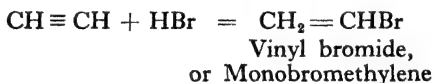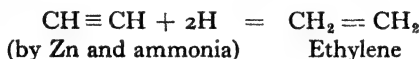
(b) *Four* atoms of hydrogen or halogen or two molecules of halogen acid to form the *paraffin* or its substitution products.

$$CH \equiv CH + 4H \quad = \quad CH_3 - CH_3$$
(by platinum black) \qquad Ethane

$$CH \equiv CH + 2HBr \quad = \quad CH_3 - CHBr_2$$
Ethylidene bromide

$$CH \equiv CH + 2Br_2 \quad = \quad CHBr_2 - CHBr_2$$
Acetylene tetrabromide
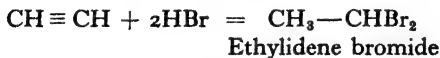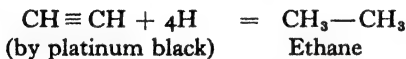
3. It reacts with ammoniacal solutions of cuprous chloride and silver nitrate to form metallic derivatives called *acetylides*, e.g. Cu_2C_2, Ag_2C_2 (white), which are explosive compounds. This serves as a delicate test for the gas.

4. It is oxidized by potassium permanganate ($KMnO_4$) to oxalic acid:

$$\begin{array}{c} CH \\ ||| \\ CH \end{array} + 2O_2 = \begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Oxalic acid
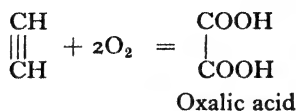
5. It is oxidized by chromic acid (CrO_3) to acetic acid:

$$\begin{array}{c} CH \\ ||| \\ CH \end{array} + \begin{array}{c} H_2 \\ || \\ O \end{array} + O = \begin{array}{c} CH_3 \\ | \\ COOH \end{array}$$

Acetic acid
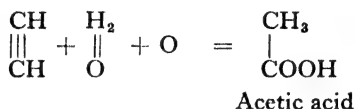
6. It combines with nitrogen under the influence of the induction spark to form hydrogen cyanide:

$$\begin{array}{c} CH \\ ||| \\ CH \end{array} + \begin{array}{c} N \\ \\ N \end{array} = 2HCN$$

7. When heated with water to 300° C. in a sealed tube, it forms acetaldehyde:

$$CH \equiv CH + H_2O = CH_3CHO$$

Acetaldehyde
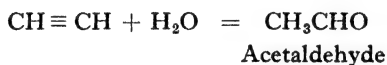
8. It yields a condensation product when led through a red-hot tube. This phenomenon is known as **polymerization**:

$$3C_2H_2 = C_6H_6$$

Benzene

Polymerization is defined as the change produced by the union of the molecules of a compound to form a new substance, which has the same percentage composition, but whose molecular weight

is a multiple of that of the parent substance, and which may easily be reconverted into the parent substance.

Constitution of the Acetylenes.

For reasons similar to those advanced in the case of the olefines, the unsaturated carbon atoms in the acetylenes are assumed to be linked by a triple bond or by treble linking.

Three formulæ are possible:

$$
\begin{array}{ccc}
\text{I} & \text{II} & \text{III} \\
\mid & \mid & \\
-CH_2 & -CH & CH \\
\mid & \mid & \mid\mid\mid \\
-C- & -CH & CH \\
\mid & \mid &
\end{array}
$$
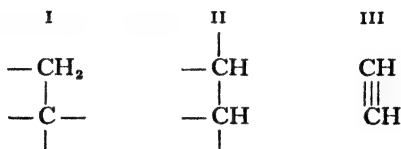
Since one unsaturated carbon atom is never found to exist alone, it must be assumed that the free valencies of the carbon atoms unite together to satisfy one another. Hence formula III is the accepted one, and this is supported by the formation of acetylene by the electrolysis of fumaric acid.

Distinguishing Tests for Hydrocarbons

Reagent	Paraffins	Olefines	Acetylenes
Bromine water	Not decolorized	Decolorized	Decolorized
Ammoniacal cuprous chloride	No action	No action	Red copper derivative
Ammoniacal silver nitrate	No action	No action	White silver derivative

Note.—Higher acetylenes in which no hydrogen atom is attached to the carbon atom with a triple bond do not give the red copper and white silver derivatives.

Baeyer's Strain Theory

Baeyer's Strain Theory has been advanced to explain the instability of compounds which contain either a double or a triple bond.

In brief, it is believed that the four valencies of the carbon atom are symmetrically arranged in space around the carbon atom, pointing towards the corners of a regular tetrahedron. Hence there is a definite angle of 109° 28′ between these valencies, which may be represented by straight lines (see fig. 19, p. 86).

If these valencies are displaced from their normal positions a strain is set up, which is directly proportional to the extent of the displacement. In the case of two carbon atoms directly united by a single bond, no displacement of the valencies occurs, but in the case of double or triple linkage displacement must occur, as shown below:

Single bond   Double bond   Triple bond
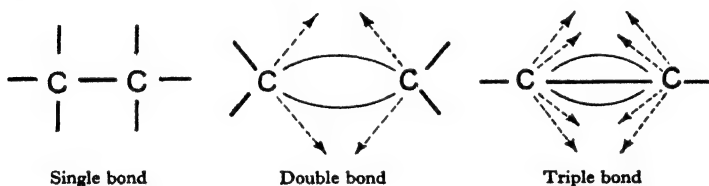
A state of strain therefore exists in the molecule, since the valencies are endeavouring to return to their normal positions. The molecule is thus in an unstable state and shows increased chemical activity. As a rule, the greater the instability of the compound, the greater the chemical activity. This is shown by the readiness with which the olefines and acetylenes combine with elements and compounds to form additive single-bond compounds. The structural representation of the formation of ethylene dibromide from ethylene and of both acetylene dibromide

and acetylene tetrabromide from acetylene may be diagrammatically represented as follows:

Ethylene (under strain)
Displacement 54° 44' inwards

Ethylene dibromide
(no strain)

Acetylene
(under strain)

Acetylene dibromide
(under strain)

Acetylene
tetrabromide
(no strain)
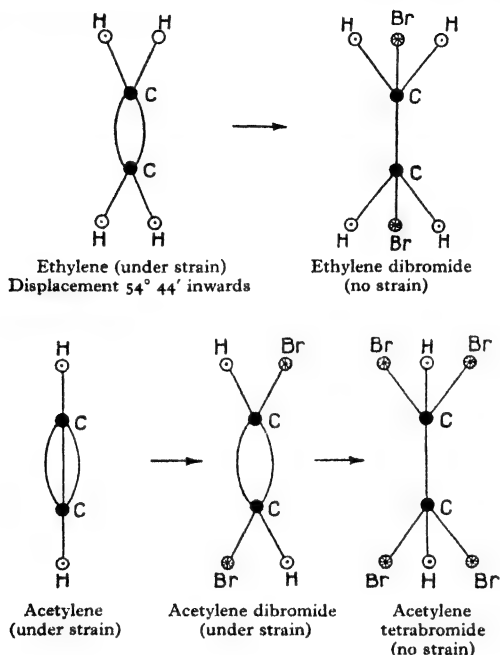
X-Ray Analysis and Molecular Structure

Laue (1912) suggested that if a crystal were composed of an orderly arrangement of atoms and molecules, it would act as a diffraction grating for X-rays, if these rays were light rays of very small wave-length. In fact, it is now computed that the spaces between the molecules in a crystal and the wave-length of X-rays are of the same order, namely 10^{-8} cm. Later Friedrich and Knipping passed a beam of X-rays through crystals and photographed the diffracted beams, which appeared on the plate as a number of spots.

Sir W. H. Bragg and W. L. Bragg used the crystal as a reflection grating. They experimented on the crystals sylvine (KCl) and rock salt (NaCl), which crystallize in the cubic system, and found that there are two strong reflections from the potassium chloride, which are due to the atoms K and Cl of approximately equal weight, whilst in the case of sodium chloride one reflection is weaker than the
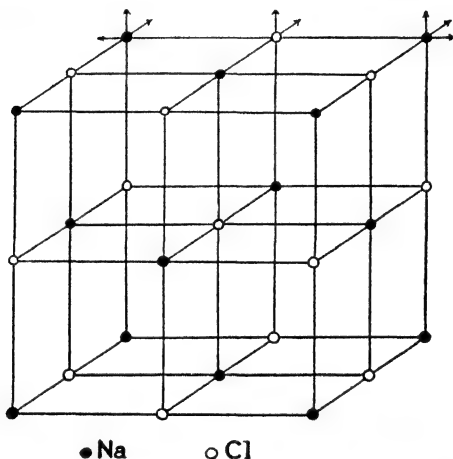
● Na   ○ Cl
Fig. 18.—Structure of Sodium Chloride Crystal

other, the weaker one being due to sodium, which has a smaller weight than chlorine. From these investigations the structure of these two compounds is indicated by the lattice structure shown in fig. 18. In the case of sodium chloride the constituent particles of the crystal are atoms (or ions) of Na and Cl arranged in a definite manner, and not molecules of NaCl.

X-ray analysis has helped to elucidate the structure of organic compounds, especially the nature of the linkages of the atoms. The study of the crystal structure of the aliphatic compounds has shown that the carbon atom is united to

four other atoms by bonds which have a tetrahedral arrangement around the carbon atom (cf. van't Hoff's tetrahedral carbon model, fig. 19).

Tetrahedron

Carbon atom spaced in Tetrahedron
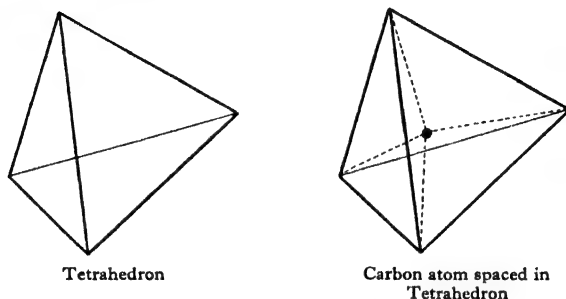
Fig. 19.—Valencies of Carbon atom indicated by dotted lines. Angle between valencies 109° 28′

QUESTIONS

1. Give two methods for the preparation of acetylene. How is acetylene converted into acetaldehyde? What is the effect of (*a*) heat, (*b*) bromine on acetylene? (*Pre. Med.*)

2. Compare and contrast the chemical behaviour of ethane and of ethylene with each of the following: hydrogen bromide, nascent hydrogen, bromine, potassium permanganate solution, sulphuric acid. Give equations where possible.

3. Mention the names and give the structural formulæ of three hydrocarbons, the molecules of which contain two atoms of carbon only.

Choosing any one of the three, describe in detail how you would prepare a jar full of the gas.

(*Civil Service: Navy, Army and Air Force.*)

4. Give two methods for the preparation of acetylene and briefly describe the properties of this substance.

What volume of oxygen would be required for the complete combustion of 10 c.c. of this gas? (*Prel. Sc.*)

5. Outline the method you would employ to prepare a quantity of pure ethylene. How, and under what conditions, does this substance react with (*a*) bromine, (*b*) sulphuric acid, (*c*) hydrogen, (*d*) hydrogen chloride?   (*Higher School Cert.*)

6. Explain by reference to the saturated hydrocarbons the meaning of each of the following: a homologous series, a general formula, isomerism, direct substitution.

7. Compare and contrast the chemical properties of olefines and paraffins.

8. The gas which bubbles up from the bottom of stagnant pools is said to consist entirely of methane. Describe in detail how you would collect a sample of this gas and treat it to verify the statement.   (*Civil Service: Customs and Excise.*)

9. Describe briefly how methane, ethylene and acetylene are prepared.

Give the names and full structural formulæ for all the possible compounds C_5H_{12}.

10. How would you obtain a current of pure dry ethylene? What is the effect on ethylene of (*a*) concentrated sulphuric acid, (*b*) chlorine, (*c*) hypochlorous acid?   (*Inter. B.Sc.(Eng.).*)

11. Give a brief description of the homologous series of hydrocarbons known as paraffins, dealing with generic formula, changes in b. pt., m. pt., &c., with change in molecular weight, natural occurrence, &c.

12. Write a clear account of the preparation, properties, and uses of acetylene.   (*Inter. B.Sc.(Eng.).*)

13. How would you pass by reactions from (*a*) methane to ethane, (*b*) ethane to butane?

Write down the structural formulæ for the pentanes.

14. How is acetylene prepared and purified? What is the action of the gas on ammoniacal solutions of (*a*) silver nitrate, (*b*) cuprous chloride, (*c*) chlorine? Explain carefully how you would prove the formula of acetylene.   (*Prel. Sc.*)

15. How would you obtain from ethyl alcohol (*a*) ethane, (*b*) ethylene?

Compare the chemical properties of ethane and ethylene.

16. How would you prepare several gas jars full of (*a*) methane, (*b*) ethylene, (*c*) acetylene?

What experiments would you make to identify the three gases if you were given the jars already filled?   (*Prel. Sc.*)

17. What is meant by the term " unsaturated compound "? Give a few examples of such substances, showing how their reactions differ from those of saturated compounds.

(*B.Sc., London, General.*)

18. Write an account of the general methods of preparation and the important chemical properties of olefines, referring to ethylene as a typical member of the series.

19. Indicate the various methods by which ethane may be obtained from an alkyl iodide.

Compare the chemical properties of ethane and ethylene.

20. Compare and contrast the chemical behaviour of the paraffin and the olefine hydrocarbons. To what do you attribute this difference?

21. Give two methods for the preparation of ethylene. Compare and contrast the properties of this substance with those of acetylene.   (*Prel. Sc.*)

22. Calculate the molecular formula of a hydrocarbon from the following experimental results:

5 c.c. of the hydrocarbon were exploded with 50 c.c. of oxygen. The volume after explosion was 40 c.c. After absorption with potash the volume was 20 c.c. (All measurements were made at room temperature.)   (*Cambridge Higher School Cert.*)

CHAPTER III

Halogen Derivatives of the Paraffins

The gaseous hydrocarbons react vigorously with chlorine and bromine in the presence of light in the cold; the higher members require heating.

The first halogen atom enters into the compound most easily, substitution becoming more difficult as the number of halogen atoms present increases.

For example, chlorine can displace the hydrogen in methane in stages:

$$
\begin{array}{ccccc}
\text{H} & \text{H} & \text{H} & \text{Cl} & \text{Cl} \\
| & | & | & | & | \\
\text{H—C—H} \rightarrow & \text{H—C—Cl} \rightarrow & \text{H—C—Cl} \rightarrow & \text{H—C—Cl} \rightarrow & \text{Cl—C—Cl} \\
| & | & | & | & | \\
\text{H} & \text{H} & \text{Cl} & \text{Cl} & \text{Cl} \\
\text{Methane} & \text{Methyl} & \text{Methylene} & \text{Chloroform} & \text{Carbon tetra-} \\
 & \text{chloride} & \text{chloride} & & \text{chloride}
\end{array}
$$
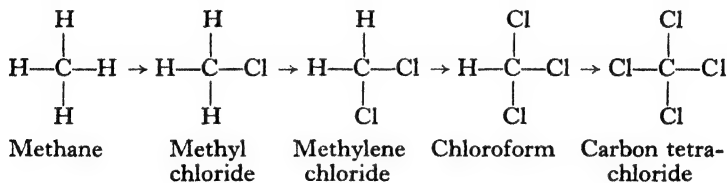
The iodine derivatives, however, cannot be obtained by direct action. The inertness of iodine is usually attributed to the liberation of hydriodic acid in the process, which by its strong reducing action immediately converts the iodine derivative back into the original paraffin. In the case of methane the reaction is represented as follows:

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$
$$CH_3I + HI \rightleftharpoons CH_4 + I_2$$
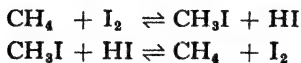
The hydriodic acid could, however, be removed by iodic acid, HIO_3, or by mercuric oxide, HgO.

The iodine derivatives of methane and ethane are repre-
sented as follows:

$$CH_4 \rightarrow CH_3I \rightarrow CH_2I_2 \rightarrow CHI_3 \rightarrow CI_4,$$
$$C_2H_6 \rightarrow C_2H_5I \rightarrow C_2H_4I_2 \cdots\rightarrow C_2I_6.$$

Fig. 20.—Preparation of Ethyl
Iodide (Reflux Condenser)

Halogen substitution products
are very sparingly soluble in water,
but readily soluble in alcohol,
ether and glacial acetic acid.

Ethyl Iodide, C_2H_5I.

Formation.—1. *Laboratory
Method.*

Ethyl iodide is prepared by
placing in a flask about 70 gm. of
ethyl alcohol and 10 gm. of red
phosphorus. To this flask is
attached an upright or reflux
condenser (fig. 20). Weigh out
about 50 gm. of iodine and add
the iodine gradually by detaching
the flask for a moment from the
condenser. A considerable evolu-
tion of heat occurs. When the
iodine has been added, the flask
is left attached to the condenser
overnight, and the contents are
then distilled from the water bath.
The distillate is shaken up with
dilute sodium carbonate or hyd-
roxide in a separating funnel (fig.
21), to remove iodine and hyd-
riodic acid. If sufficient sodium
carbonate has been used the lower
layer of ethyl iodide will be
colourless. Separate the ethyl iodide, add a few pieces of
solid calcium chloride and let stand until clear. Distil

from the water bath, using a thermometer. Collect the distillate between 70° and 75° C.

$$5C_2H_5OH + P + 5I = 5C_2H_5I + H_3PO_4 + H_2O$$

or

$$3C_2H_5OH + PI_3 = 3C_2H_5I + P(OH)_3.$$
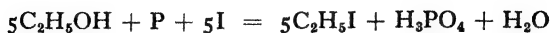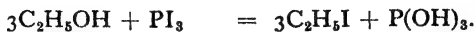
2. By the action of hydriodic acid on ethyl alcohol:

$$C_2H_5OH + HI \rightleftharpoons C_2H_5I + H_2O$$
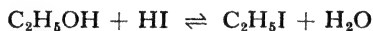
This reaction is reversible; according to the Law of Mass Action, either a large excess of halogen hydride must be used, or water must be removed by sulphuric acid or anhydrous zinc chloride.

3. By the action of hydriodic acid on ethylene:

$$C_2H_4 + HI = C_2H_5I$$

Properties. — Colourless, pleasant-smelling, highly refractive liquid. B. pt. 72° C., sp. gr. 1·94. On exposure to light it turns yellowish brown.

Reactions.

1. It is reduced by the action of a Zn–Cu couple:

$$C_2H_5I + H_2 = C_2H_6 + HI$$
$$\text{Ethane}$$

2. It reacts with sodium or zinc to form butane:

$$C_2H_5 \,|\, I + Zn + I \,|\, C_2H_5 = C_2H_5 \cdot C_2H_5 + ZnI_2$$
$$\text{Butane}$$
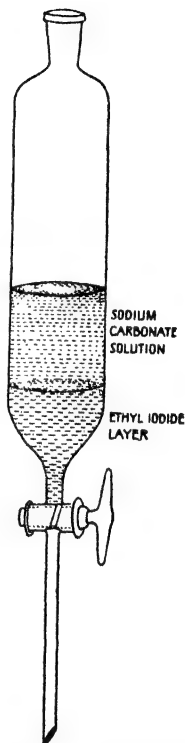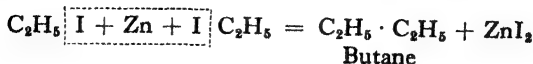
Fig. 21.—Separating Funnel. (To illustrate the separation of two immiscible liquids).

3. Excess of zinc produces zinc ethyl:

$$C_2H_5 \vdots I + 2Zn + I \vdots C_2H_5 \; = \; Zn(C_2H_5)_2 + ZnI_2$$
$$\text{Zinc ethyl}$$
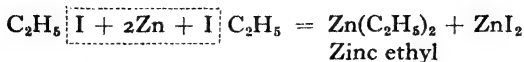
4. Aqueous alkalis, alkaline carbonates, silver oxide and litharge replace the halogen by a hydroxyl (OH) group:

$$C_2H_5I + KOH \; = \; C_2H_5OH + KI$$
$$\text{Ethyl alcohol}$$
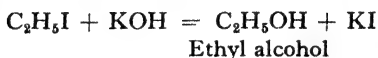
5. Alcoholic potash and dry silver oxide yield the olefine, ethylene:

$$CH_3 \cdot CH_2I + KOH \; = \; CH_2{=}CH_2 + KI + HOH$$
$$\text{Ethylene}$$
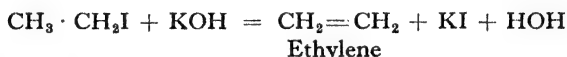
6. Sodium or potassium ethoxide yields ether:

$$C_2H_5 \vdots I + Na \vdots OC_2H_5 \; = \; C_2H_5 \cdot O \cdot C_2H_5 + NaI$$
$$\text{Ethyl ether}$$
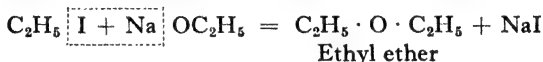
7. Alcoholic ammonia yields ethylamine (b. pt. 19°):

$$C_2H_5I + H \cdot NH_2 \; = \; C_2H_5NH_2 + HI$$
$$\text{Ethylamine}$$
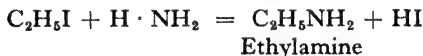
8. Potassium cyanide yields ethyl cyanide (propio-nitrile):

$$C_2H_5I + KCN \; = \; C_2H_5 \cdot CN + KI$$
$$\text{Propio-nitrile}$$
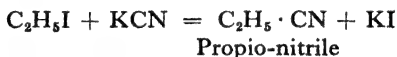
9. Potassium hydrosulphide yields ethyl mercaptan:

$$C_2H_5I + KSH \; = \; C_2H_5 \cdot SH + KI$$
$$\text{Ethyl mercaptan}$$
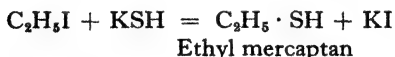
10. Potassium sulphide yields diethyl sulphide:

$$2C_2H_5I + K_2S \; = \; (C_2H_5)_2S + 2KI$$
$$\text{Diethyl sulphide}$$
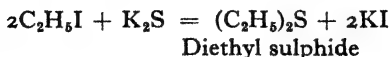
11. Silver nitrite, silver sulphate, and silver acetate

yield respectively nitro-ethane (p. 159), diethyl sulphate and ethyl acetate (b. pt. 77° C.):

$$C_2H_5I + AgNO_2 \quad = C_2H_5NO_2 + AgI,$$
$$\text{Nitro-ethane}$$
$$2C_2H_5I + Ag_2SO_4 \quad = (C_2H_5)_2SO_4 + 2AgI,$$
$$\text{Diethyl sulphate}$$
$$C_2H_5I + CH_3COOAg = CH_3 \cdot COO \cdot C_2H_5 + AgI.$$
$$\text{Ethyl acetate}$$
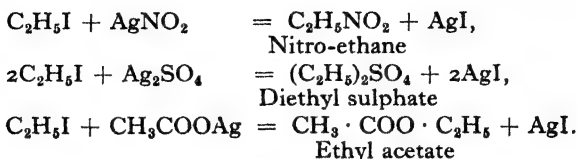
Note.—The replacement of hydroxyl by means of phosphorus halides is one of the most general reactions met with. In this way all the hydroxyl groups of aliphatic polyhydric alcohols, the hydroxyl groups of phenols, and the hydroxyl groups of all types of acids can be replaced by halogen:

$$\begin{array}{c}
CH_2OH \\
| \\
CH \cdot OH + 3PCl_5 \\
| \\
CH_2OH \\
\text{Glycerol}
\end{array} = \begin{array}{c}
CH_2Cl \\
| \\
CH \cdot Cl + 3POCl_3 + 3HCl \\
| \\
CH_2Cl \\
\text{Trichlorhydrin}
\end{array}$$

$$C_6H_5OH + PCl_5 \quad = C_6H_5Cl + POCl_3 + HCl$$
$$\text{Phenol} \qquad\qquad \text{Chloro-benzene}$$

$$3CH_3COOH + 2PCl_3 = 3CH_3COCl + P_2O_3 + 3HCl$$
$$\text{Acetic acid} \qquad\qquad \text{Acetyl chloride}$$

$$C_6H_5COOH + PCl_5 \quad = C_6H_5COCl + POCl_3 + HCl$$
$$\text{Benzoic acid} \qquad\qquad \text{Benzoyl chloride}$$
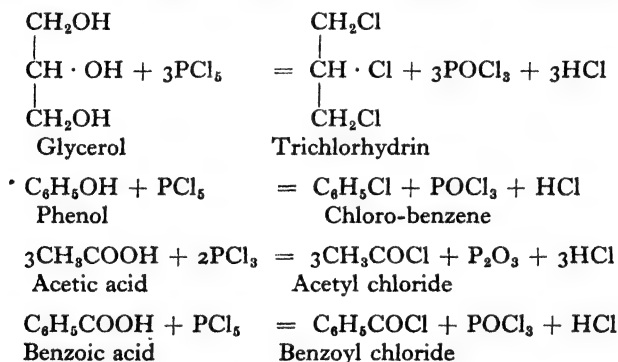
In the case of the phenols, however, the yields are unsatisfactory, owing to the phosphorus oxychloride formed as a by-product reacting with the residual phenol and giving rise to esters of phosphoric acid.

Ethyl Bromide, C_5H_2Br.

Formation.—Place 15 c.c. of alcohol in a 250 c.c. distilling flask; gradually add 12 c.c. of strong sulphuric acid, shaking and cooling the mixture under the water tap; then add 20 gm. of coarsely powdered potassium bromide and

cork the flask. Place the flask on a sand bath and connect to a water condenser. The end of the condenser should just dip under water in a boiling-tube. Arrange the apparatus so that the boiling-tube rests on the bench. Heat carefully; if the mixture tends to froth over into the condenser, remove the flame and raise the flask from the sand bath for a time. When no more oily drops distil over, pour the distillate into a measuring cylinder and read the volume of the ethyl bromide obtained. Decant off most of the water; pour the residue into a small tap funnel, add an equal volume of bench sodium carbonate solution and shake. Release the pressure by inverting the funnel and opening the tap. Separate the ethyl bromide, pour back into the funnel and shake with water. Finally run off the ethyl bromide carefully into a dry test tube, add 2 or 3 small pieces of anhydrous calcium chloride, cork and leave until clear. Decant off into a 100 c.c. distilling flask fitted with a cork and thermometer. Attach the flask to a condenser (with dry inner tube), immerse the flask in a water bath, heat carefully and collect the fraction between 35° and 42° C.

$$C_2H_5OH + H_2SO_4 = C_2H_5OSO_2OH + H_2O,$$
$$C_2H_5OSO_2OH + KBr = C_2H_5Br + KHSO_4.$$

Uses.—Ethyl bromide is used as an anæsthetic, although it has a somewhat irritating action on the lungs.

Note to Students.—It will be observed that the preparations of ethyl chloride, methyl chloride, and methyl bromide have been omitted. These compounds are normally gases, difficult to collect and to store. In answering questions on the halogen derivatives of the paraffins these compounds should never be used as examples to illustrate points of theory when substances like ethyl iodide and ethyl bromide will serve equally well.

Chloroform, $CHCl_3$.

The name chloroform is due to the fact that it was considered to be the chloride of *formyl*, the obsolete name

for the radicle ≡ CH. Liebig (1831) was the first to prepare chloroform and Simpson (1847) discovered its anæsthetic properties and introduced it into surgery.

Formation.

1. By distilling chloral (trichloracetaldehyde) with sodium hydroxide; chloroform and sodium formate are produced:

$$\begin{matrix} H \\ | \\ NaO \end{matrix} + \begin{matrix} C \cdot Cl_3 \\ | \\ C \end{matrix} \diagup^O_{\diagdown H} = \begin{matrix} CH \cdot Cl_3 \\ + \\ NaO \cdot C \end{matrix} \diagup^O_{\diagdown H} \quad (CHCl_3 + HCOONa)$$
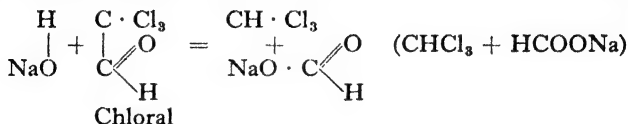
Chloral

2. From methane and methyl chloride or methylene dichloride by treatment with chlorine in sunlight.

3. (a) *On the manufacturing scale*: by boiling either ethyl alcohol or acetone with freshly-made bleaching powder and water (Liebig's method).

(b) *In the laboratory*: by boiling together 150 gm. of bleaching powder, 600 c.c. of water and 30 gm. (40 c.c. approx.) of acetone or ethyl alcohol.

Experiment.—Grind the bleaching powder into a paste with 300 c.c. of water and transfer to a large flask of capacity 2 litres. The residual bleaching powder is washed into the flask with the remaining 300 c.c. of water. Then add the ethyl alcohol or acetone. The flask is then placed on a sand bath on a tripod and is fitted to a condenser and receiver. The mixture in the flask is heated gradually, the flame being removed from time to time, as the reaction is accompanied by much frothing. When the initial reaction has subsided, the contents are boiled until no more oily drops distil with the water. The distillate is transferred to a separating funnel, shaken with dilute sodium hydroxide solution, and allowed to stand; the lower layer of chloroform is run off into a small distilling flask containing a little solid calcium chloride, and distilled from the water bath, the product boiling between 60° and 65° being collected. Yield about 20 c.c.

The reactions are based upon the action of the " available " chlorine on the organic liquid, followed by the conversion of the chlorinated compound into chloroform by the lime present in bleaching powder, as follows.

(*a*) With alcohol: chloral is first formed.
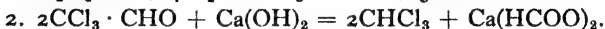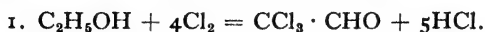
1. $C_2H_5OH + 4Cl_2 = CCl_3 \cdot CHO + 5HCl.$
2. $2CCl_3 \cdot CHO + Ca(OH)_2 = 2CHCl_3 + Ca(HCOO)_2.$
     Trichlor-   Calcium
     acetaldehyde   formate

(*b*) With acetone: trichloracetone is first formed:
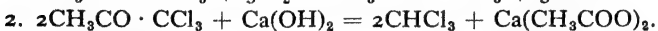
1. $CH_3 \cdot CO \cdot CH_3 + 3Cl_2 = CH_3 \cdot CO \cdot CCl_3 + 3HCl.$
2. $2CH_3CO \cdot CCl_3 + Ca(OH)_2 = 2CHCl_3 + Ca(CH_3COO)_2.$
     Trichloracetone   Calcium acetate

The complete reaction with ethyl alcohol is

$$4C_2H_5OH + 16CaOCl_2$$
$$= 2CHCl_3 + 3(HCOO)_2Ca + 13CaCl_2 + 8H_2O$$

Properties.—Colourless heavy liquid with a sweet smell and taste, b. pt. 60–62° C., m. pt. −63·2° C., sp. gr. 1·485–1·490 at 15·5° C. When pure it is neutral to litmus. It is very slightly soluble in water, but is miscible in all proportions with alcohol, ether, and benzene. It is non-inflammable. Pure dry chloroform on exposure to air and sunlight is decomposed into phosgene and chlorine:
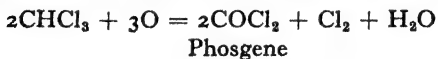
$$2CHCl_3 + 3O = 2COCl_2 + Cl_2 + H_2O$$
                    Phosgene

Chloroform of the British Pharmacopæia contains 2 per cent of added dehydrated alcohol to act as a preservative and to arrest this change.

Pure chloroform has no action on silver nitrate solution, but if any decomposition has taken place the carbonyl chloride and chlorine give a precipitate of silver chloride. Since these products are extremely toxic when chloroform is used for anæsthetic purposes, tests for purity must be

carried out in order to show that they are absent. Chloroform should be kept in dark-blue glass-stoppered bottles and protected from light.

Uses.—Chloroform is used in surgery as an anæsthetic and in medicine as a carminative (to expel wind), as a preservative, and to relieve asthma. It is also used as a solvent for rubber, gutta percha, &c., and as a cleansing agent.

Tests for Chloroform.

1. When heated with an alcoholic solution of potassium hydroxide it yields potassium formate and chloride:

$$CHCl_3 + 4KOH = H \cdot COOK + 3KCl + 2H_2O$$
<div style="text-align:center">Potassium
formate</div>
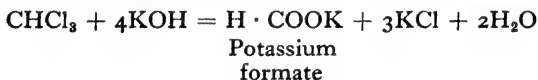
2. *Phenyl carbylamine* or *Isocyanide Reaction.* This test should be performed in a fume cupboard. Place two drops of chloroform in a test tube, add one drop of aniline and one c.c. of alcoholic potash and warm. The product has a characteristic and highly disagreeable smell of phenyl carbylamine, which is poisonous:

$$CHCl_3 + C_6H_5NH_2 + 3KOH = C_6H_5NC + 3KCl + 3H_2O$$
<div style="text-align:center">Aniline   Phenyl
carbylamine</div>
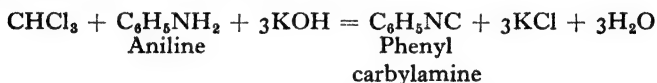
3. When it is heated with Fehling's solution (a mixture of copper sulphate solution and alkaline Rochelle salt solution (p. 527)) the latter is rapidly reduced, red cuprous oxide being precipitated:

$$CHCl_3 + 5KOH + 2CuO = Cu_2O + K_2CO_3 + 3KCl + 3H_2O$$

4. When it is mixed with a solution of α- or β-naphthol in strong caustic soda solution and heated to about 50°, a blue colour is produced, which afterwards changes to green and brown (also given by chloral and chloral hydrate).

5. Evaporate to dryness: no residue indicates purity, any residue is probably $CaCl_2$ produced in manufacture.

6. $AgNO_3$: no precipitate indicates purity; white precipitate or opalescence indicates decomposition.

7. Concentrated H_2SO_4: when shaken and allowed to stand no discoloration should take place.

8. Flame test. Introduce vapour into a Bunsen flame; green flame with characteristic noxious vapours.

Iodoform, Tri-iodomethane, CHI_3.

Formation.—1. By warming alcohol with iodine and alkali hydroxide or carbonate:

$$C_2H_5OH + 4I_2 + 6KOH = CHI_3 + HCOOK + 5KI + 5H_2O$$

The intermediate product $CI_3 \cdot CHO$, analogous to chloral, has not been isolated. On boiling with alkali, iodoform is decomposed in a similar manner to chloroform, so care must be taken in its preparation.

Experiment.—Dissolve 15 gm. of washing soda in 50 c.c. of hot water in a beaker. Cool to about 70° C. and add 8 c.c. of alcohol and 5 gm. of iodine. Stir, keeping the temperature at 70° until the mixture becomes pale yellow. Allow to cool. Iodoform separates. Filter by suction, wash well with cold water and allow to drain for a time. Transfer the iodoform and filter paper to a small beaker, dissolve the iodoform by warming with the smallest possible quantity of alcohol, filter through a fluted filter paper into a test tube, and cool. Filter off the crystals by suction; allow to drain; transfer to a watch glass and allow to dry. Take the melting-point of the specimen.

2. The *commercial method* consists in electrolysing a mixture of ethyl alcohol, potassium iodide, and sodium carbonate in solution. On electrolysis hydrogen is evolved, and iodine is liberated from the potassium iodide, which

in the presence of the alkali acts on the alcohol or acetone in the ordinary way:

$$2KI + 2H_2O = 2KOH + H_2 + I_2,$$
$$C_2H_5OH + 5I_2 + H_2O = CHI_3 + 7HI + CO_2.$$
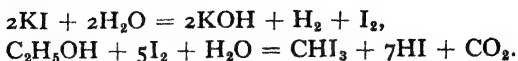
Properties.—Pale yellow lustrous crystals, crystallizing in hexagonal plates or star-shaped crystals. Characteristic odour. M. pt. 119°, sp. gr. 2. It readily sublimes and is volatile in steam. It is nearly insoluble in water, but soluble in alcohol, ether, chloroform, and carbon disulphide. When made into a paste with moist finely divided silver, it yields acetylene.

Iodoform Reaction.—This reaction serves as a delicate test for ethyl alcohol (but not methyl alcohol).

Pour a few drops of alcohol into a test tube and add about 5 c.c. of a solution of iodine in potassium iodide. To this solution add dilute sodium hydroxide solution drop by drop until the colour of the iodine just disappears. Shake up and warm very gently to about 70° C. If no turbidity or precipitate appears at once, set the test tube aside for a time. Yellow crystals of iodoform will ultimately deposit, and these may be recognized by their characteristic odour.

This reaction is also given by other substances, such as acetone, aldehyde, and substances which contain oxygen united with a $CH_3 \cdot C$— group. All ketones which contain the group $CH_3 \cdot CO$— yield iodoform under the above conditions, the —CO— group being converted into —COOH, the —CH_3 group into iodoform.

$$CH_3 \cdot CO \,|\, CH_3 + 3I_2 + 4KOH =$$
$$CH_3COOK \,|\, + CHI_3 + 3KI + 3H_2O$$
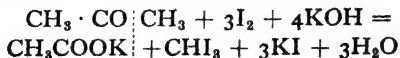
This reaction is of considerable importance and is often used for the conversion of a ketone into an acid containing one atom of carbon less than the parent substance.

Uses.—Iodoform is used in medicine and as a surgical dressing, as it prevents infection and assists the healing of wounds. Owing to its characteristic unpleasant odour it is gradually being replaced by the odourless antiseptic *iodole*.

QUESTIONS

1. Describe the preparation of chloroform. What are its chief uses? What products are formed when chloroform is exposed to the action of (*a*) air and sunlight, (*b*) caustic potash solution?   (*Pre. Med.*)

2. By what methods is ethyl iodide prepared?
How many hydrocarbons, saturated or unsaturated, can be prepared from ethyl iodide? Give the method of preparation in each case.
How would you demonstrate the presence of iodine in ethyl iodide?

3. How do each of the following substances react with potassium hydroxide: ethyl iodide, chloroform, acetic acid, ethylene dibromide?

4. Describe the method of manufacture and the chemical reactions of chloroform, and explain the tests used to control its suitability for use as an anæsthetic.

(*Chemists and Druggists Qual.*)

5. What is the action on ethyl iodide of (*a*) aqueous potassium hydroxide, (*b*) alcoholic potassium hydroxide, (*c*) moist silver oxide, (*d*) dry silver oxide?

6. By what methods may ethyl iodide be prepared? Which of these would you use in the laboratory?
By reference to this compound illustrate the usefulness of the alkyl iodides in synthetic practice.

7. State what compounds are capable of yielding chloroform on treatment with bleaching powder. Explain the course of the reactions and describe how you would prepare specimens of chloral alcoholate, chloral, chloral hydrate, and iodoform.

(*B.Sc., London, General.*)

8. Describe briefly the mode of preparation of each of the following compounds: (*a*) ethyl acetate, (*b*) formic acid, (*c*) chloroform, (*d*) ethyl iodide.

9. Describe the preparation of each of the following substances: (*a*) ethyl bromide, (*b*) ethyl iodide, (*c*) diethyl oxalate. What is the action on ethyl iodide of (i) sodium hydroxide solution, (ii) nascent hydrogen, (iii) alcoholic ammonia?

10. Determine the formula of a compound which contains 2·1 per cent of hydrogen, 12·8 per cent of carbon, and 85·1 per cent of bromine, and of which at 140° C. and 765 mm. one gram of vapour occupies 179 c.c.

How may a compound possessing this formula be obtained?

(*I. M.B., London.*)

11. Starting with ethyl alcohol, describe the preparation of chloroform. Why is it desirable for chloroform to be stored in dark bottles which should also be kept full? What is the action of potassium hydroxide on chloroform, and how would you demonstrate the presence of chlorine in this substance?

(*Pre. Med.*)

The Alcohols

Occurrence.—Different alcohols are found in nature combined with organic acids as **esters** in ethereal oils and waxes, e.g. methyl, ethyl, butyl, and amyl alcohols, and also those with 16, 27 and 30 carbon atoms. Ethyl alcohol also occurs in the free state.

The Monohydric Alcohols

The monohydric alcohols may be regarded as derived from the paraffins by the substitution of the monovalent hydroxyl group —OH for one atom of hydrogen. The monohydric alcohols form a homologous series of the general formula

$$C_nH_{2n+1}OH \text{ or } C_nH_{2n+2}O.$$
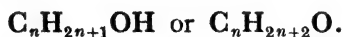
The latter formula represents a paraffin with an additional atom of oxygen. The first five members of this series are:

Methyl alcohol	CH_3OH
Ethyl alcohol	C_2H_5OH
Propyl alcohol	C_3H_7OH
Butyl alcohol	C_4H_9OH
Amyl alcohol	$C_5H_{11}OH$

Methyl Alcohol, Wood Spirit, Carbinol, CH_3OH, occurs in wood tar, and as methyl salicylate in oil of wintergreen (*Gaultheria procumbens*). The name is derived from μέθυ (*methu*), wine, and ὕλη (*ule*), wood. Wood spirit or

wood naphtha is the name given to the commercial product. It was first prepared by Boyle in 1661 by the distillation of wood-tar.

Formation.

1. By chlorinating methane and heating the methyl chloride thus formed with dilute aqueous potash in closed vessels:

$$CH_3Cl + KOH = CH_3OH + KCl$$

2. By the distillation of methyl salicylate with dilute potash:

$$C_6H_4(OH)COO \cdot CH_3 + KOH = C_6H_4(OH)COOK + CH_3OH$$

Structurally:

Methyl salicylate   Potassium salicylate
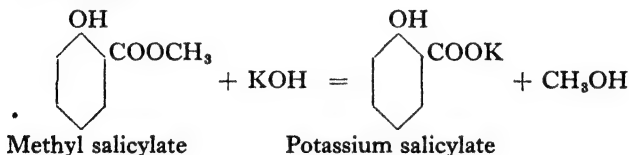
3. By the destructive distillation of wood.

Commercial Methods.—Wood (beech, birch or oak) is heated in iron retorts out of contact with air, and gases are evolved. These gases are condensed; water, methyl alcohol, acetic acid, tar and other products collect in the receiver, and wood coke or charcoal remains in the retort.

The distillate is allowed to settle; the brown aqueous layer, known as *pyroligneous liquor* or *acid*, which contains methyl alcohol, acetic acid, acetone and other substances, is drawn off from the wood-tar and distilled from a copper vessel. The vapours are passed through hot milk of lime to free them from acetic acid, and are then collected in a receiver. The acetic acid (p. 199) reacts with the lime, giving calcium acetate. The distillate is then diluted with water, and hydrocarbons and other oily impurities which are insoluble in the

dilute alcohol are thrown out of solution. The oily layer is separated by filtering through charcoal, or by standing, when it collects at the surface. The liquid is next submitted to fractional distillation, finally over quicklime, until it contains 98·99 per cent of methyl alcohol.

In order to free the methyl alcohol from acetone and other impurities it is mixed with powdered calcium chloride, with which methyl alcohol combines, forming a crystalline compound of the composition $CaCl_2 \cdot 4CH_3OH$. This substance is freed from acetone by gently heating it or by pressing it between cloths, and it is then decomposed by distilling with water; the aqueous methyl alcohol is finally dehydrated by repeated distillation with quicklime, but it still contains traces of acetone and other impurities.

Another commercial method consists in passing water gas—a mixture of carbon monoxide and hydrogen—at high pressure over chromium-manganese oxide as catalyst:

$$2CO + 4H_2 = 2CH_3OH$$
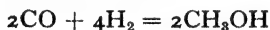
If the catalyst contains traces of an alkaline precipitant, such as rubidium or caesium hydroxide, higher alcohols are produced at the same time. For example, if the catalyst contains 15 per cent of rubidium hydroxide a mixture of compounds is obtained, the carbon being distributed as follows:

> 42 per cent carbon as methyl alcohol;
> 38 per cent carbon as other alcohols;
> 15 per cent carbon as carbonyl compounds.

4. By warming the impure compound with anhydrous oxalic acid. Methyl oxalate is produced:

$$2CH_3OH + (COOH)_2 = (COOCH_3)_2 + 2H_2O$$
Methyl oxalate
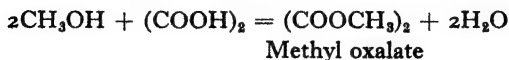
This crystalline substance is drained on the filter pump and decomposed by distillation with potash, and the aqueous

solution is then freed from water by distillation with quick-lime:

$$(COOCH_3)_2 + 2KOH = (COOK)_2 + 2CH_3OH$$
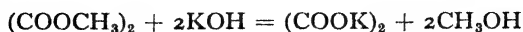
5. By treating methylamine with nitrous acid and warming the aqueous solution:

$$\begin{array}{c} CH_3 \mid N \mid H_2 \\ \mid + \mid = CH_3OH + N_2 + H_2O \\ HO \mid N \mid O \end{array}$$

Properties.—Colourless mobile liquid, sp. gr. 0·796 at 20° C., b. pt. 65° C., with an agreeable vinous or wine-like odour and a burning taste. It mixes with water in all proportions, contraction in volume taking place and heat being developed. It burns with a pale non-luminous flame, and its vapour forms an explosive mixture with air or oxygen:

$$2CH_3OH + 3O_2 = 2CO_2 + 4H_2O$$
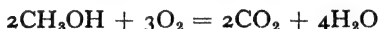
Uses.—Manufacture of certain coal-tar colouring matters; as methyl ether in the manufacture of ice; for polishes and varnishes, since it dissolves shellac and resins; as Wiggersheim's preservative liquid; for methylating spirits of wine.

Reactions.

1. It reacts with sodium and potassium to form methylates (methoxides):

$$2CH_3OH + 2Na = 2CH_3 \cdot ONa + H_2$$
$$\text{Sodium}$$
$$\text{methoxide}$$
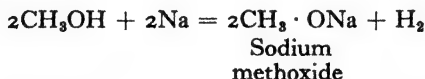
Sodium methoxide is a colourless, crystalline, very deliquescent compound, which rapidly absorbs carbon dioxide from the air and is immediately decomposed by water as follows:

$$CH_3ONa + HOH = CH_3OH + NaOH$$

2. Methyl alcohol, although neutral to litmus paper, acts as a weak base and combines with acids to form salts:

$$CH_3OH + HCl \quad = CH_3Cl + H_2O,$$
$$CH_3OH + H_2SO_4 = CH_3HSO_4 + H_2O,$$
$$2CH_3OH + H_2SO_4 = (CH_3)_2SO_4 + 2H_2O.$$
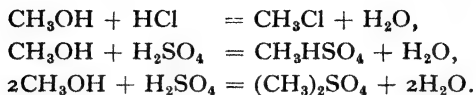
3. With bromine or iodine and red phosphorus it forms methyl bromide (CH_3Br) and methyl iodide (CH_3I) respectively.

4. With phosphorus pentachloride, trichloride, or oxychloride there is considerable development of heat and methyl chloride is formed:

$$CH_3OH + PCl_5 \quad = CH_3Cl + HCl + POCl_3,$$
$$3CH_3OH + PCl_3 \quad = 3CH_3Cl + H_3PO_3,$$
$$3CH_3OH + POCl_3 = 3CH_3Cl + H_3PO_4.$$
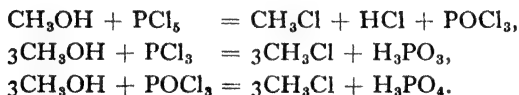
5. It is readily oxidized to formaldehyde and then to formic acid:

$$CH_3OH + O = H_2O + HCHO$$
$$\text{Formal-}$$
$$\text{dehyde}$$

$$HCHO + O = HCOOH$$
$$\text{Formic acid}$$
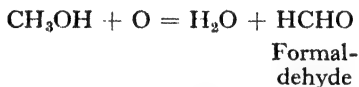
The oxidizing agents usually employed are chlorine water, bromine water, nitric acid, chromic acid, manganese dioxide and sulphuric acid, potassium permanganate or potassium dichromate and sulphuric acid. In the laboratory a red-hot coil of copper is dipped into the liquid several times, when the production of formaldehyde is easily detected by the characteristic odour of the latter.

6. When heated with a salicylate or a formate and strong sulphuric acid, methyl alcohol yields methyl salicylate or

methyl formate; these esters have odours which are fairly characteristic:

$$C_6H_4(OH)COOH + CH_3OH = C_6H_4(OH)COOCH_3 + H_2O,$$

Salicylic acid   Methyl salicylate

$$HCOOH + CH_3OH = HCOOCH_3 + H_2O.$$

Methyl formate
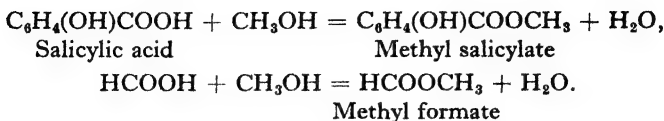
7. Pure methyl alcohol does not give the iodoform reaction, but the commercial product always contains acetone, which gives the reaction.

Tests for Methyl Alcohol are given in Chap. XXII, p. 526; Chap. XXIII, p. 537.

Constitution of the Alcohols.

The chemical behaviour of the alcohols is apparent throughout the series. In some of their reactions the alcohols resemble water; this may be illustrated by comparing the reactions of water and methyl alcohol with sodium and phosphorus halides.

Water.

    (a) $2H_2O + 2Na = 2NaOH + H_2$,

    (b) $H_2O + PCl_5 = HCl + HCl + POCl_3$,

    (c) $3H_2O + PBr_3 = 3HBr + H_3PO_3$.

Methyl Alcohol.

    (a) $2CH_4O + 2Na = 2CH_3ONa + H_2$,

    (b) $CH_4O + PCl_5 = CH_3Cl + HCl + POCl_3$,

    (c) $3CH_4O + PBr_3 = 3CH_3Br + H_3PO_3$.
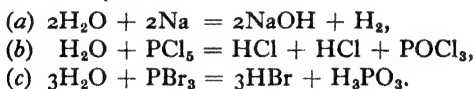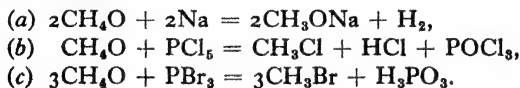
From these equations it will be observed that sodium liberates hydrogen, and in the case of the alcohol only one atom of hydrogen is liberated and replaced by sodium. Further, the decomposition of the halides of phosphorus by water and by the alcohol takes place in a similar manner.

In these reactions the radicle methyl —CH_3 acts as if it were a hydrogen atom.

In addition, the alcohols show a closer similarity with

caustic alkalis; this relationship may be illustrated by the following reactions:

Sodium Hydroxide.

$$(a) \quad NaOH + HCl \quad = NaCl + H_2O,$$
$$(b) \quad NaOH + HNO_3 = NaNO_3 + H_2O,$$
$$(c) \quad NaOH + H_2SO_4 = NaHSO_4 + H_2O.$$

Methyl Alcohol.

$$(a) \quad CH_4O + HCl \quad = CH_3Cl + H_2O,$$
$$(b) \quad CH_4O + HNO_3 = CH_3NO_3 + H_2O,$$
$$(c) \quad CH_4O + H_2SO_4 = CH_3 \cdot HSO_4 + H_2O.$$
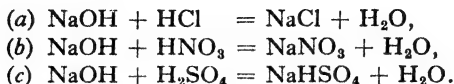
In these reactions the radicle methyl $—CH_3$ acts as if it were a sodium atom.

Constitution of Methyl Alcohol.

From the above equations it is possible to build up the graphic formula for methyl alcohol.

The empirical formula for methyl alcohol is CH_4O, and only one of its hydrogen atoms is displaced by sodium: this hydrogen atom must, therefore, be in a different state of combination from the other three. This can be represented as follows: $CH_3O(H)$.

Moreover, methyl alcohol is formed by the action of dilute alkalis on methyl chloride:

$$CH_3Cl + KOH = CH_3OH + KCl;$$

hence three of the hydrogen atoms are combined with carbon. The other hydrogen atom is not combined with carbon; hence it must be combined with oxygen, the only other alternative. The constitution of methyl alcohol is then represented as follows:

$$
\begin{array}{c}
H \\
| \\
H — C — O — H \quad \text{or} \quad CH_3OH \\
| \\
H
\end{array}
$$
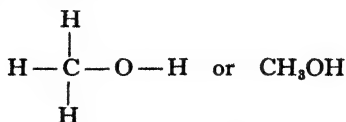
This is upheld by the following facts:

1. It is impossible to take away the oxygen atom without one of the hydrogen atoms accompanying it, e.g. action of HCl, PCl$_5$, PBr$_3$.

2. The formation of salts by the action of acids on methyl alcohol is comparable with their action on sodium hydroxide. Methyl alcohol is, in fact, methyl hydroxide.

3. One-fourth of the total hydrogen can be replaced by metallic sodium.

Ethyl Alcohol, Ethanol, Spirits of Wine, C$_2$H$_5$OH.

Occurrence.—Alcohol has been known from very early times, as it occurs in all fermented liquors, from which it was obtained by distillation. It occurs in the vegetable kingdom in combination with organic acids, e.g. ethyl butyrate, C$_3$H$_7$COOC$_2$H$_5$. It is found in the animal kingdom in diabetic urine. Small quantities of ethyl alcohol are present in wood spirit, in bone oil, and in bread (0·3 per cent).

Formation.

1. From ethane by converting it into ethyl chloride and heating the latter with dilute alkalis under pressure:

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl,$$
$$C_2H_5Cl + KOH = C_2H_5OH + KCl.$$
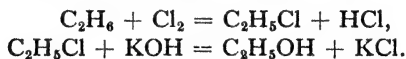
2. By passing ethylene into fuming sulphuric acid or into strong sulphuric acid at 160° C. and boiling the solution with water:

$$C_2H_4 + H_2SO_4 = C_2H_5 \cdot HSO_4,$$
$$C_2H_5 \cdot HSO_4 + HOH = C_2H_5OH + H_2SO_4.$$
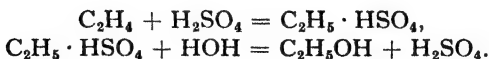
3. By reducing acetaldehyde in aqueous solution with sodium amalgam and water:

$$CH_3CHO + 2H = CH_3CH_2OH$$
Acetaldehyde
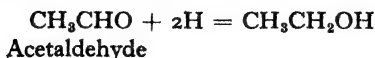
4. By the alcoholic fermentation of sugar, directly from grape and fruit sugars ($C_6H_{12}O_6$), indirectly from cane sugar ($C_{12}H_{22}O_{11}$), malt sugar, starch, &c.

Fermentation.

The name fermentation comes from the Latin *fervere*, to boil, since during the process the liberation of carbon dioxide appears to make the liquid boil. Fermentations are processes of slow decomposition of organic compounds brought about by certain substances known as **enzymes.** Enzymes are found in both animal and vegetable matter, usually in the cell sap, and are lifeless, nitrogeneous bodies of complex composition. Micro-organisms also can bring about fermentations. Among the commoner enzymes are:

Diastase, which occurs in green leaves and germinating grain and converts starch into sugar.

Ptyalin, a similar and probably identical body found in the saliva.

Pepsin, a proteolytic enzyme present in the juice of the stomach, which carries out the first stage of the hydrolysis of the proteins of food. It acts only in the fairly strong acid medium of the gastric juice. Peptone is formed from the albuminous matter.

Trypsin, which is also concerned in the digestive process. It is similar to pepsin, but in addition to peptone, leucine, tyrosine, &c., are formed by its action.

It must be noted, however, that some enzymes do not break down compounds but build them up: e.g. *lipase*, present in castor seeds, builds up ethyl acetate or glyceryl oleate under certain conditions.

The fermentation of sugar solutions for the production of alcohol is carried out by the yeast plant or other varieties of the genus *Saccharomyces*. Yeast is a unicellular fungus requiring phosphates and ammonium and potassium salts

for its sustenance; it propagates by gemmation or budding
and contains in its cell sap three enzymes, namely, *zymase*,
invertase and *maltase*.

When yeast is added to a solution of grape or cane sugar
the liquid soon begins to froth and has the appearance of
boiling, although no perceptible rise of temperature occurs.
This process (fermentation) is due to the enzyme zymase,
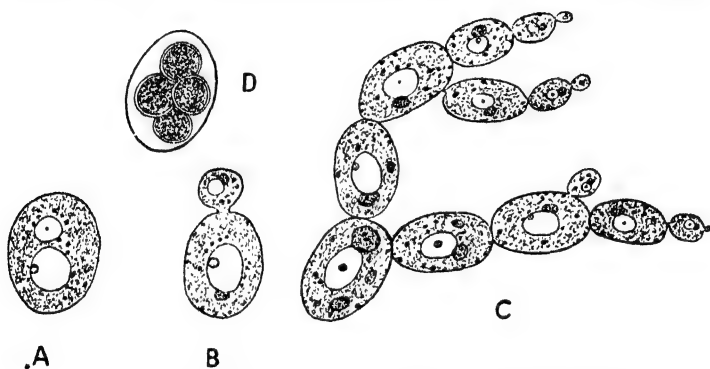
Fig. 22.—*Saccharomyces Cerevisiae*, the yeast plant (highly magnified)

A, Yeast Cell, showing the nuclear vacuole.   B, Yeast Cell budding.   C, A colony
of living cells of brewers' yeast.   D, Ascus or cell which has formed four thick-
walled spores.

a yellowish liquid found in the yeast, which converts the
grape sugar as follows (Buchner):

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$
Grape sugar
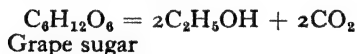
In the case of cane sugar the enzyme invertase in the
yeast first converts this sugar into a mixture of glucose and
fructose:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
Cane sugar   Glucose   Fructose

The glucose and fructose thus formed are eventually con-
verted to alcohol by the zymase.

During the fermentation process about 95 per cent of

the sugar is converted into alcohol and carbon dioxide, but other products are formed at the same time. These products include glycerol, $C_3H_5(OH)_3$ (2·5–3·6 per cent), succinic acid, $C_4H_6O_4$ (0·4–0·7 per cent), and fusel oil.

Fusel oil consists of the higher homologues of ethyl alcohol, e.g. amyl, propyl, and butyl alcohols, and esters, &c.

Conditions of Fermentation.

1. *Temperature:* The best working temperature is between 25° and 30° C.; beyond this temperature yeast gradually loses its activity and at 60° C. it is rendered inactive.

2. *Alcoholic content:* The percentage of alcohol must not exceed 14 per cent; a more concentrated solution destroys the organism.

3. *Reagents:* Acids, alkalis, alcohol, mercuric chloride, and antiseptic substances such as chloroform, thymol, carbolic acid, must not be present or be added, otherwise the yeast plant is rendered inactive.

4. *Yeast:* This fungus must be freshly prepared and moist. The activity of yeast is destroyed if it is thoroughly dried.

5. *Substitutes:* Zymase extract can be employed instead of yeast. The advantage is that zymase extract can be preserved by antiseptics, e.g. chloroform, and hence can be stored until required.

The following carbohydrates are used for the preparation of alcohol and alcoholic liquors by the fermentation process. The enzyme employed for conversion is given in brackets.

A. Glucose (grape sugar), found in grapes, and fructose (fruit sugar), found in ripe fruits, are converted by the ferment zymase in yeast:

$$C_6H_{12}O_6 \ = \ 2C_2H_5OH + 2CO_2$$
Glucose or
Fructose
(Zymase)
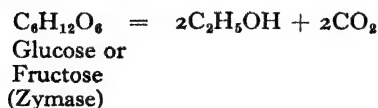
The alcoholic liquor obtained is used for making wines.

B. Cane sugar, beet sugar, and beet sugar molasses are first converted by the ferment invertase into glucose and fructose, which are then acted upon by the ferment zymase, which is also found in yeast:

$$\underset{\substack{\text{Cane sugar}\\\text{(Invertase)}}}{C_{12}H_{22}O_{11} + H_2O} = \underset{\substack{\text{Glucose}\\\text{(Zymase)}}}{\begin{array}{c}CH_2OH\\|\\CHOH\\|\\(CHOH)_3\\|\\CHO\end{array}} + \underset{\substack{\text{Fructose}\\\text{(Zymase)}}}{\begin{array}{c}CH_2OH\\|\\(CHOH)_3\\|\\CO\\|\\CH_2OH\end{array}}$$
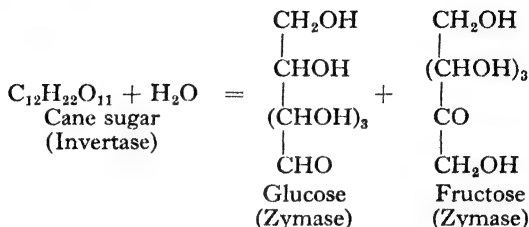
The alcoholic liquor obtained is used for making brandy.

C. Starch from cereals and potatoes is converted into alcohol by the action of three ferments.

The starch is first converted into dextrine and malt sugar by the ferment *diastase*, found in germinating barley.

$$\underset{\substack{\text{Starch or}\\\text{Cellulose}\\\text{(Diastase)}}}{3\,(C_6H_{10}O_5)_n} + nH_2O = \underset{\substack{\text{Dextrine}\\\text{(Zymase)}}}{(C_6H_{10}O_5)_n} + \underset{\substack{\text{Malt sugar}\\\text{(Maltase)}}}{nC_{12}H_{22}O_{11}}$$
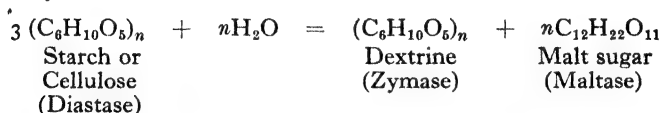
This reaction may also be induced by boiling starch or cellulose with dilute mineral acids.

The malt sugar is converted into grape sugar by the ferment *maltase*, found in yeast or in malt. Finally the dextrine and grape sugar are acted upon by the third ferment *zymase*, which converts them into alcohol. Alcoholic liquors obtained from cereals are used for making beer and brandy, those from potatoes for making potato brandy and industrial spirit.

Manufacture of Beer, &c.

Barley is first soaked in water and allowed to germinate until a small shoot appears, when the life of the grain

is destroyed by heating it in malt kilns. The product is known as **malt.** The malt is then placed in warm water and the starch present undergoes fermentation by the enzyme diastase, being converted into malt sugar. The action of the diastase is arrested after a short interval, so that only a portion of the starch in the barley is converted; the extract, known as **wort,** is drawn off, run into copper pans and boiled with hops. The hot liquid is cooled rapidly in stone vats, yeast is added to ferment the sugar until from 4 to 6 per cent of alcohol is present, when the action is stopped, and beer results.

Further fermentation gives more alcohol, which when distilled gives **whisky.**

French Brandy is made by distilling alcohol from wine.

Rum is the distillate from fermented molasses.

Wine is made from fermented grape juice.

Absolute Alcohol is made by repeated fractional distillation and finally distillation over quicklime. It usually still contains a small amount of water.

Methylated Spirits is denatured alcohol containing about 10 per cent of wood spirit, castor oil, or other adulterant (p. 117).

Properties of Ethyl Alcohol.

Colourless mobile liquid, with a fragrant odour, b. pt. 78·3° C., m. pt. −112·3° C., sp. gr. 0·7936 at 15° C. It is hygroscopic and is miscible with water and ether in all proportions. The presence of a trace of water in absolute alcohol is determined by pouring a few drops of the alcohol (*a*) into benzene or paraffin, when a slight opalescence is observed; (*b*) on to white anhydrous copper sulphate, which is tinged blue. These tests are not given by water-free alcohol.

The most important reactions of alcohol may be summarized as follows:

REAGENT	PRODUCT
1. Chlorine, Bromine.	Chloral CCl_3CHO; bromal CBr_3CHO.
2. Bleaching powder and water.	Chloroform $CHCl_3$.
3. Iodine and alkali	Iodoform CHI_3.
4. The halogen acids, HCl, HBr, HI.	Ethyl chloride; bromide; iodide. C_2H_5Cl C_2H_5Br C_2H_5I
5. Bromide or iodine and red phosphorus.	Ethyl bromide or Ethyl iodide.
6. Concentrated sulphuric acid:	
(a) ordinary conditions;	(a) Ethyl hydrogen sulphate $C_2H_5HSO_4$.
(b) at 130°–140° with excess alcohol;	(b) Ether $(C_2H_5)_2 \cdot O$.
(c) at 160° with excess acid.	(c) Ethylene C_2H_4.
7. Concentrated nitric acid.	Ethyl nitrate $C_2H_5NO_3$.
8. Dilute nitric acid.	Glycollic acid CH_2OH $\mid$ COOH
9. Potassium dichromate and sulphuric acid, or manganese dioxide and sulphuric acid.	Acetaldehyde CH_3CHO
10. Chromium trioxide.	Takes fire and burns to CO_2 and H_2O.
12. Red hot platinum wire held in vapour.	Acetaldehyde CH_3CHO.
12. Platinum black and alcohol vapour exposed to air.	Acetic acid CH_3COOH.
13. Alcoholic potash.	Brown solution of aldehyde resin.
14. Acetic acid.	Ethyl acetate $CH_3COOC_2H_5$.
15. Acetyl chloride.	Ethyl acetate.

Tests for Alcohol (see also Chap. XXII, p. 525, and Chap. XXIII, p. 533).

Alcohol may be detected:

1. By the iodoform reaction (p. 99).

2. By means of benzoyl chloride, C_6H_5COCl, which yields with alcohol the characteristic-smelling ethyl benzoate; or *p*-nitrobenzoyl chloride, which yields ethyl *p*-nitrobenzoate (m. pt. 57°):

COCl

+ C_2H_5OH =

NO_2

p-nitrobenzoyl
chloride

$COOC_2H_5$

+ HCl

NO_2

Ethyl *p*-nitro-
benzoate
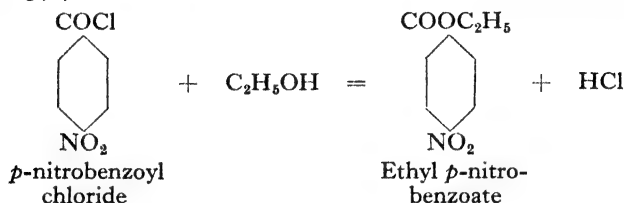
The constitutional formula of ethyl alcohol may be arrived at by the same process as that described for methyl alcohol.

For Practice.—On what grounds is the structural formula for ethyl alcohol represented as follows?

$$\begin{array}{ccc} & H & H \\ & | & | \\ H-&C-&C-OH. \\ & | & | \\ & H & H \end{array}$$
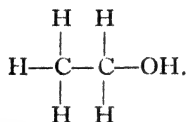
Preparation of Official Alcohols

For the preparation of official alcohols 95 per cent alcohol is used and the following volumes in millilitres are diluted to one litre to make an alcohol of the required strength.

Alcohol	Millilitres	Specific Gravity	Alcohol	Millilitres	Specific Gravity
90%	948	0·833	50%	526	0·934
80%	842	0·864	45%	474	0·943
70%	737	0·890	25%	363	0·971
60%	632	0·913	20%	210	0·976

Absolute alcohol has a specific gravity of 0·7936 at 15·5° C.

Rectified spirit contains 90 per cent of ethyl alcohol by volume and has a specific gravity of 0·833 and is 58° over proof (see below).

The B.P. 1932 points out that when alcohol is mixed with water both a contraction in volume and a rise in temperature are observed; hence, only the cooled liquid should be employed.

The greatest contraction takes place when 47·7 volumes of distilled water are mixed with 52·3 volumes of alcohol; the resulting volume is 96·35 volumes, i.e. there is a contraction of 3·65 per cent by volume.

Methylated Spirits.

There are four varieties of methylated spirits, in accordance with various Acts of Parliament and Regulations which the Customs and Excise Commissioners authorize.

1. *Industrial Methylated Spirit* is a mixture containing 95 parts by volume of alcohol (95 per cent.) and 5 parts by volume of approved wood naphtha (methyl alcohol). It is known as " 66 O P. Industrial Methylated Spirits ", and its specific gravity must not exceed 0·817.

Proof Spirit acquired its name from being the weakest alcohol which could ignite a little gunpowder moistened with it. Proof spirit contains 57·10 per cent of ethyl alcohol by volume at 60° F., or 49·28 per cent by weight. Pure Absolute Alcohol is 75·35° over proof. Alcohol 43° over proof contains 81·58 per cent of alcohol by volume.

2. *Industrial Methylated Spirit* (pyridinized) has the same composition as No. 1 but with the addition of 0·5 per cent of crude pyridine.

3. *Mineralized Methylated Spirit* has the following composition by volume:

> 90·0 per cent of rectified spirits,
> 9·5 per cent of wood naphtha,
> 0·5 to 1 per cent of crude pyridine.

To every 100 gall. of the mixture 0·375 gall. of petroleum oil and not less than $\frac{1}{40}$ oz. of methyl violet or other powdered aniline dye are added.

4. *Power Methylated Spirit* consists of 92 per cent of alcohol, 2·5 per cent by bulk of wood naphtha, 0·5 per cent of crude pyridine, and at least 5 per cent of petrol or benzol.

To every 100 gall. of this mixture $\frac{1}{40}$ oz. of spirit red III dye is added.

Alcoholometry is the name given to the method of determining the quantity of alcohol in fermented liquors. The method employed consists in taking the specific gravity of the liquid by a special form of hydrometer known as Sikes's hydrometer. The quantity of alcohol corresponding to different specific gravities is then read off from official tables. (See Appendix, p. 643.)

Use of Alcohol in Biological Work

Absolute alcohol is used in practical instruction in biology for fixing and hardening tissues, and for dehydrating tissues before mounting them for microscopical examination.

Alcohol denatured with pyridine is useless for histological work, as pyridine causes a nuclear contraction which cannot, as has been claimed, be successfully combated even with the use of acetic acid.

The alternative use of industrial spirit, C_2H_5OH with 5 per cent of CH_3OH, is not of great value, even if it is supplied in absolute strength with no admixture of benzene or other

adulterant, since a reducing effect on the tissues frequently occurs. The same objection applies to the use of methyl alcohol of absolute strength alone. For some methods in histology absolute methyl alcohol can be used, but for a great deal of work no substitute for absolute ethyl alcohol has yet been found. Any attempt to use a substitute results in the tissues being so altered that the student is presented with a completely false impression of them.

Any denatured spirit which gives the slightest trace of a precipitate on the addition of water is useless, since precipitation will occur inside the cells of tissues and the purpose of their examination under the microscope, i.e. the elucidation of the true nature of the cellular contents, is defeated. It is essential that absolute (ethyl) alcohol should be used for dehydration.

In preparing tissues for microscopic examination they have to be impregnated with a preparation of the gum of *Abies balsamifera* of the correct refractive index for the material in order to make it translucent. The solvent for this gum is xylene, and the tissues must, as a preliminary, be infiltrated with xylene. Xylene is intolerant of even the smallest trace of water (it is, in fact, a delicate test reagent used to detect the smallest quantities of water) and hence complete dehydration with absolute alcohol is required before xylene is used. If all traces of moisture are not removed the tissue remains opaque and cannot be studied. Further, as a method of biological analysis of tissues, microchemical reactions are utilized for determining and correlating morphological and functional differences. Differential staining reactions are employed, involving the use of two or more stains of definite chemical action. The vehicle for the last stain used in a differential series is frequently clove oil, which is intolerant of even small amounts of moisture, so that here also complete dehydration with absolute alcohol is necessary.

These processes are routine methods in biological work and form an integral part of instruction in biology.

Alcohol is also used for preserving anatomical specimens, since it has the property of coagulating albumin.

Primary, Secondary, and Tertiary Alcohols

As in the case of the paraffin hydrocarbons, it is possible to build up the alcohol series of compounds theoretically by substituting a methyl ($-CH_3$) group for a hydrogen atom, disregarding in every case the hydrogen atom in the hydroxyl ($-OH$) group.

Methyl alcohol   gives   Ethyl alcohol

In the case of ethyl alcohol the hydrogen atoms are not all attached to the carbon atoms in the same manner. One carbon atom has three attached hydrogen atoms, while the other has two hydrogen atoms. Hence when a methyl group is produced it is possible to obtain two isomeric compounds, namely Normal or Primary propyl alcohol and Isopropyl or Secondary propyl alcohol:

Ethyl alcohol
b. pt. 78°
sp. gr. 0·806

Normal propyl alcohol
b. pt. 97°
sp. gr. 0·817

Isopropyl alcohol
b. pt. 81°
sp. gr. 0·789
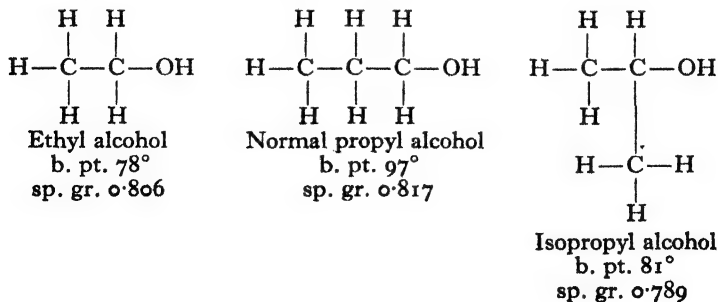
Again, it is possible to obtain four isomeric compounds of the same molecular formula from the propyl alcohols by substituting a methyl group for a hydrogen atom.   Two are formed from the normal alcohol and two from the iso-propyl alcohol:

I (a)

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH$$

Normal butyl alcohol
b. pt. 117°; sp. gr. 0·823

I (b)

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{C}-OH$$

$$H-\overset{\displaystyle \dot{C}}{\underset{\underset{\displaystyle H}{|}}{}}-H$$

Primary isobutyl alcohol
b. pt. 107°; sp. gr. 0·806

II

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{C}-OH$$

$$H-\overset{\displaystyle C}{\underset{\underset{\displaystyle H}{|}}{}}-H$$

Secondary butyl alcohol
b. pt. 100°

Primary Alcoholic Group Structure

$$-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH \quad \text{or} \quad -CH_2OH$$

A monovalent group
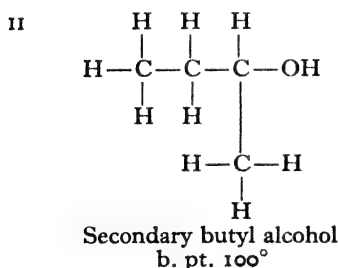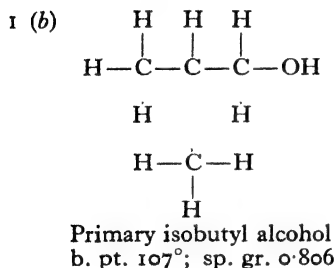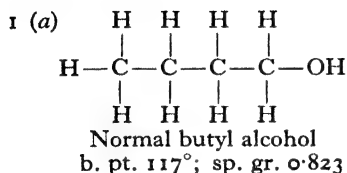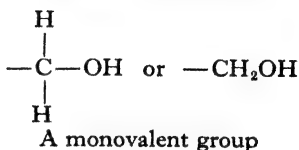
A Primary Alcohol contains the hydroxyl group attached to a carbon atom united to at least two other hydrogen atoms.

Secondary Alcoholic Group Structure

$$-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle |}{}}{C}}-OH \quad \text{or} \quad \diagdown CH \cdot OH \diagup$$
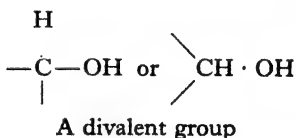
A divalent group

A Secondary Alcohol contains the hydroxyl group attached to a carbon atom united to one hydrogen atom only.

III

$$
\begin{array}{c}
\text{H} \\
| \\
\text{H}\!-\!\overset{\displaystyle |}{\underset{\displaystyle |}{\text{C}}}\!-\!\text{H} \\
\text{H} \\
| \\
\text{H}\!-\!\overset{\displaystyle |}{\underset{\displaystyle |}{\text{C}}}\!-\!\overset{\displaystyle |}{\underset{\displaystyle |}{\text{C}}}\!-\!\text{OH} \\
\text{H} \\
| \\
\text{H}\!-\!\overset{\displaystyle |}{\underset{\displaystyle |}{\text{C}}}\!-\!\text{H} \\
\text{H}
\end{array}
$$
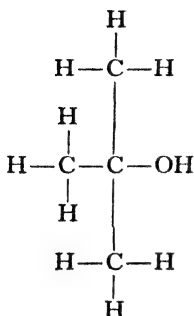
Tertiary butyl alcohol
b. pt. 83°; sp. gr. 0·786

Tertiary Alcoholic Group Structure

$$-\overset{\displaystyle |}{\underset{\displaystyle |}{\text{C}}}-\text{OH}$$
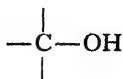
A trivalent group

A Tertiary Alcohol contains the hydroxyl group attached to a carbon atom to which no hydrogen atoms are united.

Example—Find the structural formulæ of the seven isomeric amyl alcohols $C_5H_{11}OH$. Name them if possible (see p. 125).

The three classes of alcohols may be distinguished by:

(A) Oxidation Test,
(B) Victor Meyer's Test.

A. Oxidation Test.

Primary Alcohols form **aldehydes** containing the **same** number of carbon atoms as the original alcohol:

$$CH_3OH + O = HCHO + H_2O \longrightarrow HCOOH$$
Formaldehyde   Formic acid

$$CH_3CH_2OH + O = CH_3CHO + H_2O \longrightarrow CH_3COOH$$
Acetaldehyde   Acetic acid
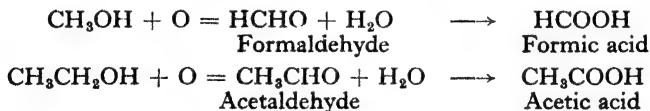
The aldehydes are easily oxidized to acids also containing the **same** number of carbon atoms.

Secondary Alcohols form **ketones** containing the **same** number of carbon atoms as the original alcohol:

$$\begin{array}{l} CH_3 \\ \diagdown \\ CH\cdot OH + O = \\ CH_3 \diagup \end{array} \quad \begin{array}{l} CH_3 \\ \diagdown \\ CO + H_2O \longrightarrow \\ CH_3 \diagup \end{array} \quad CH_3COOH$$

Secondary propyl alcohol   Acetone   Acetic acid
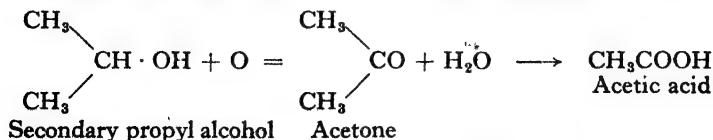
The **ketones** are difficult to oxidize, but on further

oxidation yield acids containing a **smaller** number of carbon atoms.

Tertiary Alcohols give **ketones** containing a **smaller** number of carbon atoms than the original alcohol:

$$CH_3\!\!\diagdown \atop CH_3\!\!-\!\!C\!\!-\!\!OH + 2O_2 = \quad CH_3\!\!\diagdown \atop CH_3\!\!\diagup CO + CO_2 + 2H_2O$$

Tertiary butyl alcohol   Acetone
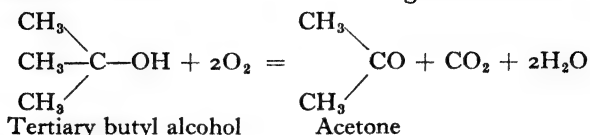
For practical details, see Chap. XXIII, p. 537.

B. Victor Meyer's Test.

This consists in first converting the alcohol into an alkyl halide and then treating the halide with silver nitrite so as to form a nitro-compound (p. 159). The compound thus formed, when acted upon by nitrous acid, yields a characteristic derivative. These reactions may be illustrated by taking the butyl alcohols as examples.

Reagent	Primary	Secondary	Tertiary
	$C_3H_7CH_2OH$	C_3H_8CHOH	$C_3H_9C \cdot OH$
HI	$C_3H_7CH_2I$ Normal butyl iodide	C_3H_8CHI Secondary butyl iodide	C_3H_9CI Tertiary butyl iodide
AgNO$_2$	$C_3H_7CH_2NO_2$ Nitrobutane	$C_3H_8CHNO_2$ Secondary nitrobutane	$C_3H_9C \cdot NO_2$ Tertiary nitro-butane
HNO$_2$	$C_3H_7 \cdot C\!\!-\!\!NO_2$ $\parallel$ NOH Butyl nitrolic acid. The H of the NOH group is acidic and can react with NaOH to form a **blood red** sodium compound	$C_3H_8C\!\!-\!\!NO_2$ $\parallel$ NO Butyl pseudo-nitrol. A **blue** compound	No reaction

Formation of Alcohols (General)

Primary.

1. By reducing aldehydes with sodium amalgam and water:

$$CH_3CHO + 2H = CH_3CH_2OH$$

2. By saponification or hydrolysis of their esters:

$$CH_3COOC_2H_5 + KOH = CH_3COOK + C_2H_5OH$$

Note.—The term **hydrolysis** is applied to a chemical change involving the addition of the elements of water. The term **saponification** is applied particularly to the hydrolysis of esters, of which the ordinary process of soap-making (p. 232) is a special case.

3. By warming the alkyl halides with water, moist silver oxide, or silver acetate:

$$C_2H_5I + HOH = C_2H_5OH + HI,$$
$$C_2H_5I + AgOH = C_2H_5OH + AgI,$$
$$C_2H_5I + CH_3COOAg + HOH = C_2H_5OH + CH_3COOH + AgI.$$
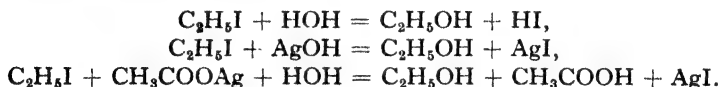
4. By treating primary amines with nitrous acid:

$$C_2H_5 \cdot NH_2 + HNO_2 = C_2H_5OH + N_2 + H_2O$$
Ethylamine
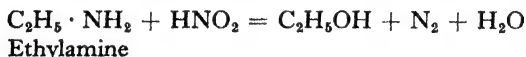
Secondary.

1. By replacing the hydroxyl groups of polyhydric alcohols by halogen atoms, and then reducing the halogen derivative:

$$C_3H_5(OH)_3 \xrightarrow{\text{(HCl)}} C_3H_5Cl_2(OH) \xrightarrow{\text{(H)}} C_3H_7OH$$
Glycerol   Dichlorhydrin   Isopropyl alcohol
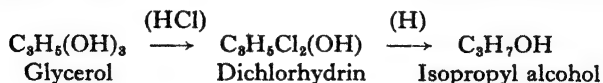
2. By reducing ketones with sodium amalgam:

$$CH_3COCH_3 + 2H = CH_3 \cdot CHOH \cdot CH_3$$
Acetone   Isopropyl alcohol
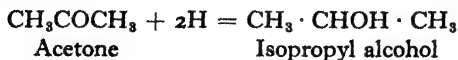
Tertiary.

By the action of Grignard reagents (magnesium alkyl halides (p. 477)) on (*a*) acid chlorides, (*b*) esters of organic acids, (*c*) ketones, and decomposing the products with water:

(*a*) $CH_3COCl + 2CH_3MgBr = (CH_3)_3CO \cdot MgBr + MgBrCl$,

(*b*) $CH_3COOC_2H_5 + 2CH_3MgBr$
$$= (CH_3)_3CO \cdot MgBr + MgBrOC_2H_5,$$

$$(c) \quad \underset{CH_3}{\overset{CH_3}{\diagdown}} CO + CH_3MgBr = CH_3 - \underset{CH_3}{\overset{CH_3}{\diagup}} CO \cdot MgBr.$$
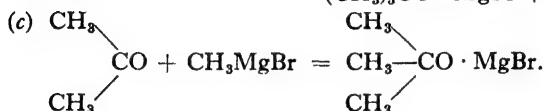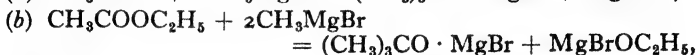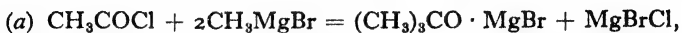
Hydrolysis gives the tertiary alcohol:

$$CH_3 - \underset{CH_3}{\overset{CH_3}{\diagup}} CO \cdot MgBr + HOH = CH_3 - \underset{CH_3}{\overset{CH_3}{\diagup}} C \cdot OH + MgBrOH.$$

Tertiary butyl
alcohol
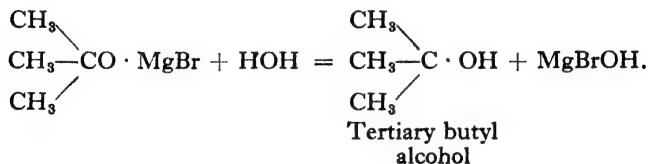
Nomenclature

In naming the alcohols it is best to refer them to methyl alcohol, just as the hydrocarbons are referred to methane. Methyl alcohol is called *carbinol*:

Methyl alcohol	HCH_2OH	Carbinol
Ethyl alcohol	CH_3CH_2OH	Methyl carbinol
Primary propyl alcohol	$C_2H_5CH_2OH$	Ethyl carbinol
Secondary propyl alcohol	$(CH_3)_2CHOH$	Dimethyl carbinol
Tertiary butyl alcohol	$(CH_3)_3COH$	Trimethyl carbinol, &c.

The alcohols may thus be regarded as substitution products of methyl alcohol.

QUESTIONS

1. How would you obtain a sample of absolute ethyl alcohol from cane sugar?

Write equations to show the action of (*a*) sodium, (*b*) phosphorus pentachloride, (*c*) concentrated sulphuric acid, (*d*) chromic acid, (*e*) concentrated hydriodic acid on ethyl alcohol, and point out how these reactions are useful in establishing a constitutional formula for the alcohol. (*Civil Service: Executive Group.*)

2. In what chemical reactions does ethyl alcohol resemble (*a*) water, (*b*) sodium hydroxide?

What do you understand by a primary, a secondary, and a tertiary alcohol? Give one example of each type.

3. How do the following substances react together:

(*a*) ethylene and sulphuric acid;

(*b*) acetylene and ammoniacal silver nitrate;

(*c*) acetamide and phosphorus pentoxide;

(*d*) ethyl alcohol, phosphorus, and iodine?

4. What general methods are available for the preparation of primary, secondary, and tertiary alcohols respectively? What experiments would you make if you had to determine whether a given alcohol was a primary, a secondary, or a tertiary alcohol? (*Phar. Chem. Qual.*)

5. Why is the structural formula of ethyl alcohol written $CH_3 \cdot CH_2 \cdot O \cdot H$? How would you prepare from ethyl alcohol specimens of (*a*) iodoform, (*b*) acetaldehyde?

6. Starting with ethyl alcohol, indicate briefly, giving formulæ, how each of the following may be prepared: ethylene bromide, ethyl iodide, iodoform, acetic aldehyde.

7. Define the following:

(*a*) Absolute alcohol.

(*b*) Alcohol.

(*c*) Rectified spirit.

(*d*) Industrial methylated spirit.

State briefly the purposes for which they are used in pharmacy. (*Chemists and Druggists Qual.*)

8. Write an account of the various ways in which alcohol can be oxidized, explaining how the products vary with the conditions, and how you could identify them.

9. Compare and contrast the chemical behaviour of ethylene and ethyl alcohol with each of the following: nascent hydrogen, hydrogen chloride, sodium, concentrated sulphuric acid, an oxidizing agent.

10. Indicate by means of equations the general methods of preparation of primary, secondary, and tertiary alcohols, and show how these three classes differ from each other in their chemical reactions. Give examples of primary, secondary, and tertiary alcohols of pharmaceutical importance.

(Chemists and Druggists Qual.)

11. What is the characteristic or active group of the alcohols? How do the properties of the alcohols vary with the position of this group in the carbon chain?

12. Give a concise, reasoned statement showing the evidence which leads to the accepted constitutional formula for ethyl alcohol. What substances are formed when ethyl alcohol is heated (*a*) with concentrated sulphuric acid, (*b*) with a mixture of concentrated sulphuric acid and potassium bromide, and (*c*) with a mixture of concentrated sulphuric acid and acetic acid? *(Inter. B.Sc.)*

13. Explain briefly the methods used for the manufacture of (*a*) methyl alcohol, (*b*) ethyl alcohol.

Illustrate by means of equations the general chemical properties of alcohols of this type. *(Chemists and Druggists Qual.)*

14. Write a short account of the formation of ethyl alcohol by fermentation. *(II. M.B., London.)*

15. Describe two methods by which methyl alcohol is obtained on the large scale. Set out logically the evidence upon which its formula rests. By what chemical reactions would you distinguish between methyl alcohol and ethyl alcohol?

(Inter. B.Sc., London.)

16. Describe the series of reactions by which ethyl alcohol can be synthesized from methyl alcohol.

17. Enumerate the steps by which ethyl alcohol is prepared from substances containing starch.　How does ethyl alcohol react with (*a*) sulphuric acid, (*b*) bleaching powder?

(Cambridge Higher School Cert.)

18. An organic compound was found on analysis to contain 64·8 per cent of carbon, 13·6 per cent of hydrogen, and 21·6 per cent of oxygen, and its vapour density was found to be 37. The compound liberated hydrogen when treated with sodium. Write down possible graphical formulæ for the compound and explain the tests you would make to ascertain which was the correct one.　　　*(Cambridge Higher School Cert.)*

19. Starting with ethyl alcohol, indicate briefly, giving formulæ, how each of the following may be prepared: ethylene bromide, ethyl iodide, iodoform, acetaldehyde.

20. What products are obtained by the oxidation of ethyl alcohol and of iso-propyl alcohol?

How may these alcohols be re-formed from their oxidation products?

21. Briefly summarize with the aid of chemical equations the general methods of formation and the general chemical reactions of (*a*) monohydric alcohols, (*b*) alkyl halides.

(Chemists and Druggists Qual.)

22. Write down the constitutional formulæ of methyl alcohol and of its oxidation products　Name them.

Derivatives of the Alcohols

A. Esters or Alkyl Salts.
B. Ethers or Alkyl Oxides.
C. Nitrogen Bases or Amines.
D. Nitro-paraffins.

A. ESTERS

Esters are formed by the action of an alcohol on an organic or inorganic acid, a reaction which is superficially similar to the formation of *salts* by the action of a base on an acid. Esters may therefore be termed *alkyl salts*.

Ethyl alcohol and acetic acid give ethyl acetate, while sodium hydroxide and acetic acid give sodium acetate:

$$CH_3CO \cdot OH + HO \cdot C_2H_5 \rightleftharpoons CH_3CO \cdot OC_2H_5 + H_2O,$$
$$CH_3CO \cdot OH + HO \cdot Na \quad = CH_3CO \cdot ONa + H_2O.$$
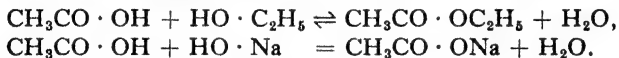
These reactions, although analogous, are not identical. The first reaction is known as Esterification, the second reaction as Neutralization.

Esterification is the process by which an ester is produced by the direct action of an acid with an alcohol. It differs from neutralization in two respects:

1. In neutralization the reaction, as a rule, is complete and irreversible, and is obtained when an acid is added to a base until a change is shown by an appropriate indicator. In esterification the reaction is a reversible or balanced one, and never proceeds to completion. The water formed during the reaction has a tendency to hydrolyse the ester and reform the original products. The formation of ethyl

acetate in the above reaction ceases when 66 per cent of the acid is converted into the ester (provided, of course, that equivalent quantities are employed. A larger quantity of alcohol will convert more of the acid into the ester.)

2. In esterification the reaction proceeds slowly; in some cases several hours elapse before the acid is more or less converted into the ester. This is due to the fact that the alcohols are weak bases and the organic acids are weak acids and that neither ionize to any great extent.

In order to increase the velocity of the reaction and to obtain a larger yield of the ester, a catalytic agent is used, e.g. dry hydrochloric acid, concentrated sulphuric acid, or anhydrous zinc chloride.

Ultra-violet light also accelerates the reaction between alcohols and organic acids.

The following formulæ represent a series of ethyl salts; the ethyl group can be replaced by other alkyl groups:

$$O\Big\langle {}^{CHO}_{C_2H_5} \qquad O\Big\langle {}^{NO}_{C_2H_5} \qquad O\Big\langle {}^{NO_2}_{C_2H_5} \qquad O\Big\langle {}^{SO_2(OH)}_{C_2H_5} \qquad {}^{Cl}_{C_2H_5}$$

| Ethyl formate | Ethyl nitrite | Ethyl nitrate | Ethyl hydrogen sulphate | Ethyl chloride |
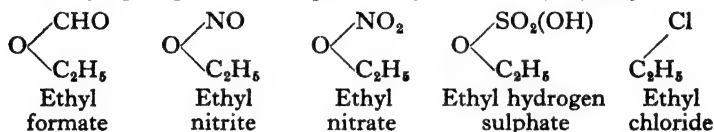
It will be observed that in the alkyl esters the alkyl group is united by oxygen to the acidic radicle. Note that the substitution products (e.g. ethyl chloride) and additive products of the hydrocarbons are also esters. These esters, known as halide esters, contain an alkyl group directly attached to the acid radicle, and are usually discussed separately.

The general formula of the esters of the fatty acids is

$$C_nH_{2n}O_2 \text{ or } C_nH_{2n+1} . COO . C_mH_{2m+1}$$

HCOOCH₃
$$HCOOCH_3$$
Methyl formate

$$HCOOC_2H_5$$
Ethyl formate

$$CH_3COOCH_3$$
Methyl acetate

$$CH_3COOC_2H_5$$
Ethyl acetate

$$C_2H_5COOCH_3$$
Methyl propionate

$$C_2H_5COOC_2H_5$$
Ethyl propionate
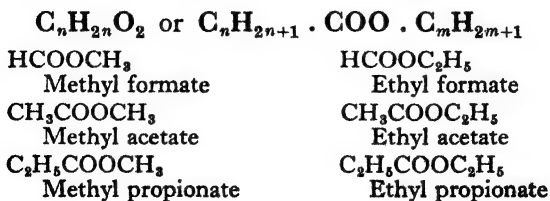
Ethyl Acetate, Acetic Ether, $CH_3COOC_2H_5$.

Formation.—1. By heating a metallic salt of acetic acid with an ethyl halide:

$$CH_3COO\overline{|Ag + I|}C_2H_5 = CH_3COOC_2H_5 + AgI$$
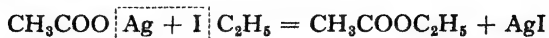
2. By heating ethyl alcohol with glacial acetic acid. The action is reversible, but proceeds to completion if a dehydrating agent is added to remove the water formed:

$$CH_3COO\overline{|H + OH|} \cdot C_2H_5 \rightleftharpoons CH_3COOC_2H_5 + H_2O$$
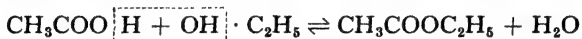
In the laboratory two methods are in use, depending on different dehydrating agents.

Method 1.—(Concentrated sulphuric acid as dehydrating agent.)

Procedure.—Pour into a 500 c.c. distilling flask 50 c.c. of ethyl alcohol and then add cautiously 75 c.c. of concentrated sulphuric acid, with constant shaking and cooling. The neck of the flask is fitted with a thermometer and tap funnel whose stem is drawn out to a fine point which dips under the liquid mixture. The flask is connected to a Liebig condenser and the contents are gently heated on a sand tray to 140° C. A mixture of equal volumes of alcohol and glacial acetic acid is placed in the tap funnel and added to the liquid in the flask at the same rate as that at which the distillate collects. About 250 c.c. of the mixture are added and the temperature is kept at 140° C. throughout the experiment, the bulb of the thermometer being immersed in the liquid.

The distillate is then purified by transferring it to a separating funnel and shaking it with sodium carbonate solution of reagent strength. The aqueous lower layer is run off and the process repeated until the upper layer of ethyl acetate is neutral to litmus. The ester is then shaken with brine solution to remove alcohol, and this solution is run off as completely as possible. The ester is then dehydrated by pouring it into a small distillation flask containing

about 25 gm. of solid calcium chloride, allowing it to stand and then distilling from the water bath (fig. 23). The portion boiling between 74° and 79° C. is collected.

The reaction appears to take place in two stages:

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O,$$
$$C_2H_5HSO_4 + CH_3COOH = CH_3COOC_2H_5 + H_2SO_4.$$
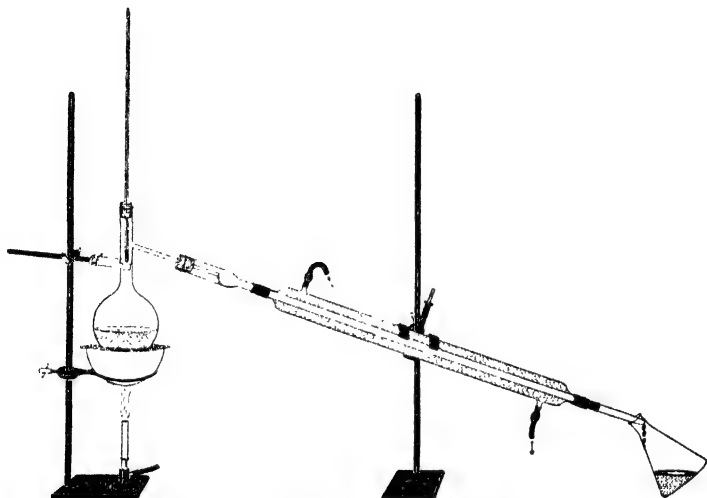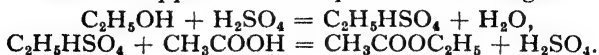
Fig. 23.—Distillation from the Water Bath

Theoretically the sulphuric acid is capable of converting a large quantity of alcohol and acetic acid into the ester but as the acid becomes diluted the yield diminishes in time.

Method 2.—(Hydrogen chloride as dehydrating agent.)

Procedure.—A 500 c.c. flask containing 30 c.c. of alcohol is weighed. An apparatus is then fitted up for the generation of hydrogen chloride (from common salt and sulphuric acid), which is dried by passing it through concentrated sulphuric acid contained in a Drechsel bottle. The dry gas is then bubbled through the alcohol until it has increased in weight by about 9 gm. During the passage of the gas the flask is cooled by running water. When this increase in weight has been obtained 30 c.c. of glacial acetic acid are added to

the mixture and the contents of the flask are heated for half an hour on the water bath, using a reflux condenser.

The reactions are as follows:

$$C_2H_5OH + HCl \rightleftharpoons C_2H_5Cl + HOH,$$
$$C_2H_5Cl + HOH + CH_3COOH = CH_3COOC_2H_5 + HCl + HOH.$$
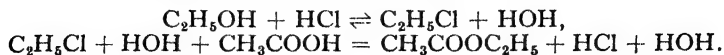
The ethyl acetate is then purified as described under Method 1. The hydrogen chloride reacts with the water formed during the reaction, giving a very strong acid, and so prevents the reaction becoming reversible.

3. By treating acetyl chloride or acetic anhydride with alcohol:

$$CH_3CO \cdot \overline{Cl + H} \, O \cdot C_2H_5 = CH_3COOC_2H_5 + HCl,$$

$$\begin{matrix} CH_3CO \\ \diagdown \\ \diagup \\ CH_3CO \end{matrix} O + HOC_2H_5 = CH_3COOC_2H_5 + CH_3COOH.$$

Acetic anhydride
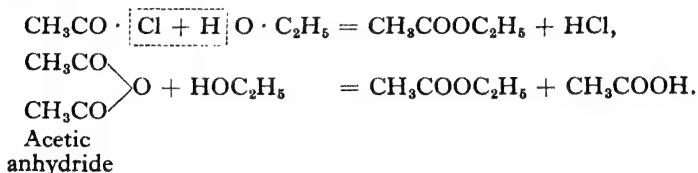
Properties.

Colourless mobile liquid with a pleasant fruity odour, b. pt. 77° C. It is specifically lighter than water and slightly soluble in water, though not miscible with it. If ethyl acetate is allowed to stand in contact with water, the water will ultimately redden blue litmus.

It is miscible with alcohol, chloroform and ether in all proportions.

Ethyl acetate is readily hydrolysed by hot alkalis, more slowly by hot mineral acids and by water:

$$CH_3COO \cdot C_2H_5 + KOH = CH_3COOK + C_2H_5OH$$
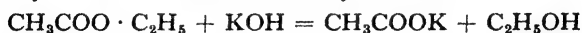
When treated with concentrated ammonia it forms acetamide and alcohol:

$$CH_3CO \, \overline{O \cdot C_2H_5 + H} \, NH_2 = CH_3CONH_2 + C_2H_5OH$$
Acetamide
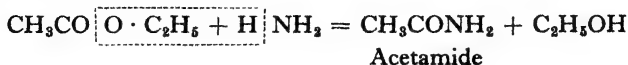
The production of ethyl acetate is used to detect the presence of acetic acid or of an alkyl acetate (p. 530).

Uses.—It is much used as a synthetic agent in chemistry, e.g. in the manufacture of antipyrine (for treatment of fever, rheumatism, neuralgia, &c.), also for perfuming fruit juices, &c., and in medicine.

Methyl Acetate, CH_3COOCH_3, is made in precisely the same way as ethyl acetate, using methyl alcohol in laboratory method 1 above. The product is fractionated and the portion between 57° and 63° C. collected.

Aceto-acetic Ester, $CH_3 . CO . CH_2 . COOC_2H_5$.

This ester is a derivative of the very unstable aceto-acetic acid, $CH_3 \cdot CO \cdot CH_2 \cdot COOH$.

Ethyl aceto-acetate, or aceto-acetic ester, is formed when sodium ethoxide acts on ethyl acetate. The condensation is a particular case of a general reaction known as *Claisen's reaction.* Two molecules of ethyl acetate condense, one molecule of alcohol being eliminated in the process:

$$\begin{array}{c} CH_3-C-\overline{|OC_2H_5|} \\ \| \qquad \quad \\ O \; + \; |H|CH_2-COOC_2H_5 \end{array} = \begin{array}{c} CH_3-C-CH_2 \cdot COOC_2H_5 \\ \| \\ O \qquad + \; C_2H_5OH \\ \text{Ethyl aceto-acetate} \end{array}$$
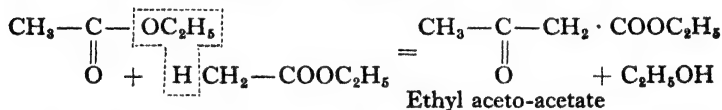
Since either sodium or sodium ethoxide is used to form the ester, the reaction may be more completely elucidated as follows:

Ethyl acetate in all probability contains a trace of alcohol, which first reacts with the sodium, for a gradual effervescence begins, increasing as the action proceeds, the gas evolved being hydrogen:

(1) $2C_2H_5OH + 2Na = 2C_2H_5ONa + H_2$
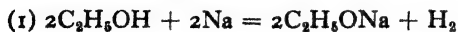
The sodium ethoxide then reacts with ethyl acetate to form an additive sodium compound:

$$(2) \; CH_3-C\!\!\begin{array}{c} \diagup OC_2H_5 \\ \diagdown O \end{array} + C_2H_5ONa = CH_3-C\!\!\begin{array}{c} \diagup OC_2H_5 \\ -OC_2H_5 \\ \diagdown ONa \end{array}$$
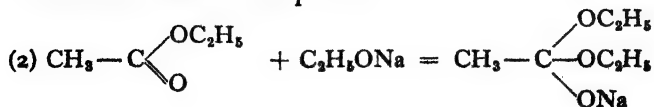
This additive compound then reacts with another molecule of ethyl acetate to form the sodium salt of ethyl aceto-acetate and alcohol; the latter may react with fresh sodium as in stage (1):

$$(3)\ CH_3 - \overset{\displaystyle OC_2H_5}{\underset{\displaystyle ONa}{C}} - OC_2H_5 + H - \overset{\displaystyle H}{CH} \cdot COOC_2H_5$$

$$= CH_3 - \underset{\displaystyle ONa}{C} = CH \cdot COOC_2H_5 + 2C_2H_5OH$$
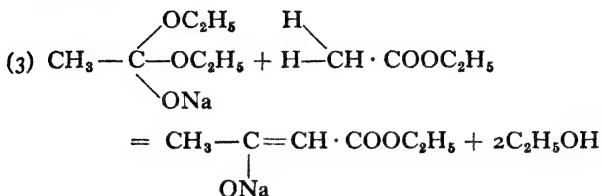
From this sodium salt the free ester is liberated by the addition of acetic acid, followed by the fractional distillation under reduced pressure of the oil which separates:

$$(4)\ CH_3 - \underset{\displaystyle ONa}{C} = CH \cdot COOC_2H_5 + HOOC \cdot CH_3$$

$$= CH_3 - \underset{\displaystyle O}{\overset{\displaystyle \|}{C}} - CH_2 \cdot COOC_2H_5 + CH_3COONa$$
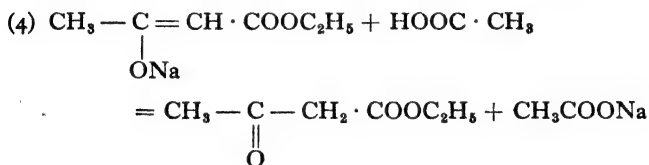
Ethyl aceto-acetate is a colourless liquid with a pleasant fruity smell (b. pt. 181° C.). It gives a violet coloration with an alcoholic solution of ferric chloride. Aceto-acetic acid is found in the urine during starvation and diabetes; it is never found unless acetone is present. Aceto-acetic acid gives a cherry-red colour with a 10 per cent ferric chloride solution (Gerhardt's test). This test is not given by acetone.

Tests for Aceto-acetic Ester are given in Chap. XXII, p. 531.

Uses of Ethyl Aceto-acetate in Synthesis.

This ester contains a methylene —CH_2— group between two carbonyl groups. In the group —CO—CH_2—CO— the hydrogen atoms of the CH_2 group possess acidic

properties. Hence they are replaceable by metallic sodium, but not simultaneously. Substitution can take place in two stages, as follows:

(1) $2CH_3 — \underset{\underset{O}{\|}}{C} — CH_2 \cdot COOC_2H_5 \quad 2CH_3 \cdot \underset{\underset{O}{\|}}{C} — CHNaCOOC_2H_5$
$+ 2Na \qquad\qquad + H_2$
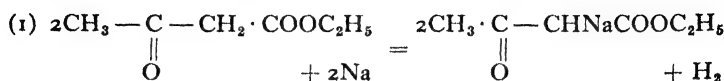
This sodium derivative is then treated with an alkyl derivative, e.g methyl iodide; a mono-alkyl derivative is formed, which can be acted upon by a second atom of sodium:

$CH_3 \cdot \underset{\underset{O}{\|}}{C} — CHNa \cdot COOC_2H_5 \quad CH_3 \cdot \underset{\underset{O}{\|}}{C} — CH \cdot CH_3 \cdot COOC_2H_5$
$+ CH_3I \qquad\qquad\qquad + NaI$

Mono-alkyl derivative

(2) $2CH_3 — \underset{\underset{O}{\|}}{C} — CH \cdot CH_3 \cdot COOC_2H_5 + 2Na$

$= 2CH_3 — \underset{\underset{O}{\|}}{C} — CNaCH_3 \cdot COOC_2H_5 + H_2$

$CH_3 — \underset{\underset{O}{\|}}{C} \cdot CNa \cdot CH_3COOC_2H_5 + CH_3I$

$= CH_3 \cdot \underset{\underset{O}{\|}}{C} — \overset{\diagup CH_3}{\underset{\diagdown CH_3}{C}} — COOC_2H_5 + NaI$

Di-alkyl derivative
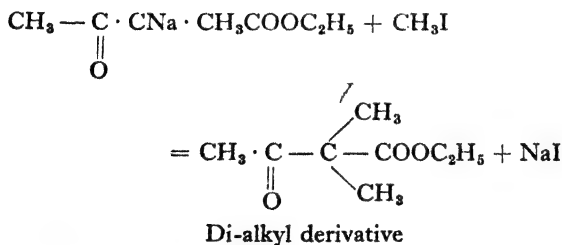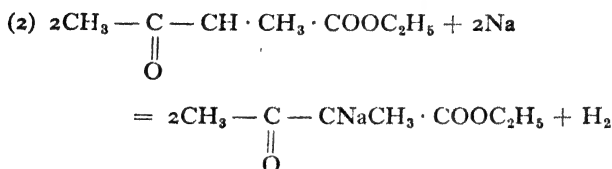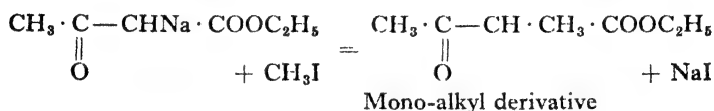
Ethyl aceto-acetate and its alkyl derivatives can undergo two kinds of hydrolysis, according to the strength of the alkali used:

A. **Ketonic hydrolysis,** in which ketones are formed, is brought about by dilute aqueous or alcoholic alkalis.

One molecule of water is involved in the reaction:

$$\begin{array}{c}
CH_3CO\ CH_2 | CO | O\ C_2H_5 \\
| + | \\
H\ | O\ | H
\end{array} = CH_3 \cdot CO \cdot CH_3 + CO_2 + C_2H_5OH$$
Acetone

$$\begin{array}{c}
CH_3CO\ CH\ CH_3 | CO | O\ C_2H_5 \\
| + | \\
H | O\ | H
\end{array} = \begin{array}{c} CH_3CO\ CH_2 \cdot CH_3 + CO_2 \\ \text{Methyl} \quad + C_2H_5OH \\ \text{ethyl ketone} \end{array}$$

$$\begin{array}{c}
CH_3CO\ C(CH_3)_2 | CO | O\ C_2H_5 \\
| + | \\
H | O\ | H
\end{array} = \begin{array}{c} CH_3CO \cdot CH(CH_3)_2 + CO_2 \\ \text{Methyl} \quad + C_2H_5OH \\ \text{isopropyl ketone} \end{array}$$
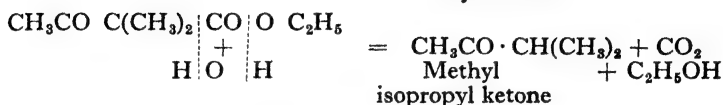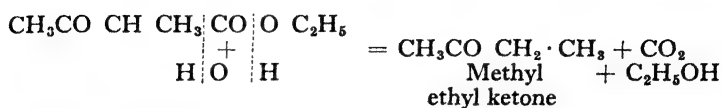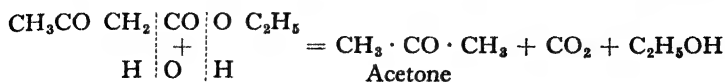
B. **Acid hydrolysis,** in which fatty acids are formed, is brought about by concentrated alcoholic alkalis.

Two molecules of water are involved in the reaction:

$$\begin{array}{c}
CH_3CO | CH_2CO | O\ C_2H_5 \\
| | \\
HO | H + OH | H
\end{array} = \begin{array}{c} 2CH_3COOH + C_2H_5OH \\ \text{Acetic acid} \end{array}$$

$$\begin{array}{c}
CH_3CO | CH\ CH_3CO | OC_2H_5 \\
| | \\
HO | H + \quad OH | H
\end{array} = \begin{array}{c} CH_3COOH + CH_3 \cdot CH_2COOH \\ \text{Acetic acid} \quad \text{Propionic acid} \\ + C_2H_5OH \end{array}$$
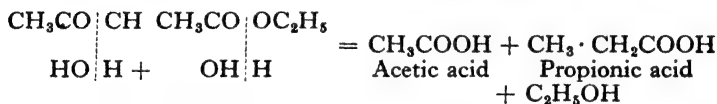
From these reactions it is clear that by means of aceto-acetic ester, synthesis of

(*a*) substituted esters of the aceto-acetic ester type,
(*b*) a series of ketones,
(*c*) a series of acids

can be effected.

Ethyl Sulphates.

Sulphuric acid, being a dibasic acid, can form two classes of esters with alkyl radicles, which correspond to the acid and normal metallic sulphates. For example,

Ethyl hydrogen sulphate, $C_2H_5HSO_4$, corresponds to $KHSO_4$,
Diethyl sulphate, $(C_2H_5)_2SO_4$, corresponds to K_2SO_4.

Ethyl Hydrogen Sulphate, Ethyl Sulphuric Acid, $C_2H_5HSO_4$.

Formation.—1. By passing ethylene into fuming sulphuric acid or into hot ordinary sulphuric acid:

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + \begin{matrix} HO \\ \\ HO \end{matrix}\Big\rangle SO_2 = \begin{matrix} CH_3 \\ | \\ CH_2 \cdot O \cdot SO_2OH \end{matrix} \quad \text{or} \quad O\Big\langle\begin{matrix} C_2H_5 \\ \\ SO_2OH \end{matrix}$$
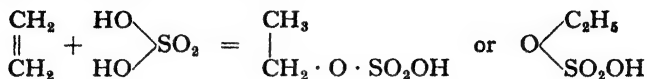
2. By heating alcohol with concentrated sulphuric acid:

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$$

The laboratory method consists in heating equal volumes of alcohol and acid at 100° C. on a water bath for an hour. The solution is then cooled and a slight excess of barium carbonate added; excess of sulphuric acid is precipitated as barium sulphate and barium ethylsulphate is left in solution:

$$2C_2H_5HSO_4 + BaCO_3 = Ba(C_2H_5SO_4)_2 + CO_2 + H_2O$$

The excess of barium carbonate and the precipitated barium sulphate are filtered off. Sulphuric acid is then added slowly to the filtrate until a precipitate of barium sulphate is no longer observed. This precipitate is then filtered off and the filtrate evaporated under reduced pressure at the ordinary temperature; by this means both alcohol and water are got rid of, leaving the ethyl hydrogen sulphate as a thick liquid:

$$Ba(C_2H_5SO_4)_2 + H_2SO_4 = 2C_2H_5HSO_4 + BaSO_4$$

Properties.—A colourless oily liquid. It is a monobasic acid like potassium hydrogen sulphate, forming salts with bases and carbonates:

$$C_2H_5HSO_4 + KOH = C_2H_5KSO_4 + HOH.$$

The alkali, barium, lead and calcium ethylsulphates are soluble in water (in the last three cases contrast the sulphates).

The importance of ethyl hydrogen sulphate lies in the fact that it is an intermediate product in the conversion of ethylene into (*a*) alcohol, (*b*) ether.

(*a*) It reacts with:

(1) boiling water; hydrolysis takes place and ethyl alcohol is formed:

$$C_2H_5HSO_4 + HOH = C_2H_5OH + H_2SO_4;$$
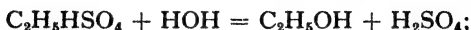
(2) hot alcohol, to form diethyl ether:

$$C_2H_5HSO_4 + C_2H_5OH = C_2H_5 \cdot O \cdot C_2H_5 + H_2SO_4;$$
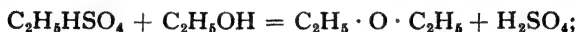
(3) concentrated sulphuric acid, or when heated alone, to form ethylene:

$$C_2H_5HSO_4 = C_2H_4 + H_2SO_4;$$

(4) hot methyl alcohol, to form the mixed ether, methyl ethyl ether:

$$C_2H_5HSO_4 + CH_3OH = CH_3 \cdot O \cdot C_2H_5 + H_2SO_4.$$
$$\text{Methyl ethyl ether}$$
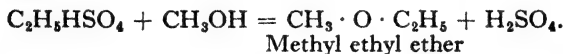
Diethyl sulphate, $(C_2H_5)_2SO_4$, is formed by warming ethyl iodide with silver sulphate:

$$2C_2H_5I + Ag_2SO_4 = (C_2H_5)_2SO_4 + 2AgI$$
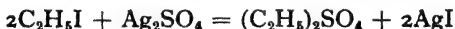
It is a colourless liquid, b. pt. 208° C.

B. Ethers

The ethers are substances which contain two alkyl groups such as CH_3—, C_2H_5—, C_3H_7—, united by an oxygen atom. They are related to the metallic oxides in the same way as the alcohols are to the metallic hydroxides.

$$C_2H_5OH \text{ corresponds to KOH,}$$
$$C_2H_5OC_2H_5 \text{ corresponds to KOK.}$$

Ethers are subdivided into

(*a*) Simple Ethers;
(*b*) Mixed Ethers.

Simple ethers are those produced when two similar radicles form the compound, e.g. $C_2H_5 . O . C_2H_5$, Ethyl ether.

Mixed ethers are those produced when two different radicles form the compound, e.g. $C_2H_5 . O . CH_3$, Methyl ethyl ether.

The ethers are *isomeric* with the alcohols and have the general formula

$$C_nH_{2n+2}O.$$
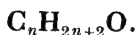
Dimethyl ether, $CH_3 . O . CH_3$, is isomeric with ethyl alcohol, C_2H_5OH.

Ethyl ether, $C_2H_5 . O . C_2H_5$, is isomeric with butyl alcohol, C_4H_9OH.

The following is a brief comparison of the properties of the ethers with those of alcohols of the same molecular weight:

Ethers	Alcohols
Colourless and neutral.	Colourless and neutral.
More volatile; e.g. dimethyl ether, a gas, b. pt. $-23°$ C.;	Less volatile; e.g. ethyl alcohol, a liquid, b. pt. $78°$ C.;
Ethyl ether, b. pt. $35°$ C.	Butyl alcohol, b. pt. $116°$ C.
Lower specific gravity; e.g. ethyl ether, sp. gr. 0.723.	Higher specific gravity; e.g. butyl alcohol, sp. gr. 0.810.
Only slightly soluble in water.	Lower members soluble in water.
No action with sodium.	Form alcoholates with sodium.
No action with PCl_5.	Form alkyl chlorides with PCl_5.

Ethyl ether, $C_2H_5 . O . C_2H_5$, was discovered by Valerius Cordus in 1544 (by Method 2, ii, p. 141).

Formation.—1. By warming ethyl iodide with sodium ethoxide:

$$C_2H_5 | I + Na | O \cdot C_2H_5 = C_2H_5 \cdot O \cdot C_2H_5 + NaI$$
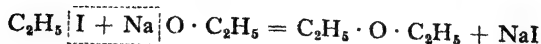
2 By laboratory methods.

Warning: Ether is **highly inflammable,** so great care must be exercised in its preparation. On no account may the receiver containing ether be placed near a naked flame. Moreover, ether vapour is heavy and has a tendency to flow along a bench, hence all lights must be extinguished when the receiver is detached.

Method (*i*).—Required 4 gm. sodium,
                        50 c.c. pure alcohol,
                        10 c.c. ethyl iodide.

Procedure.—The alcohol is placed in a flask fitted with a reflux condenser. Cut the sodium into thin slices and drop it through the mouth of the condenser into the alcohol. When the sodium has dissolved pour in the ethyl iodide and heat the mixture on the water bath for 10 minutes. Sodium iodide separates out. The contents are then distilled from the water bath with the condenser in the normal position; ether and alcohol collect in the receiver, which is cooled by ice. The distillate is then transferred to a separating funnel and shaken with strong brine solution, which dissolves the alcohol, leaving an upper layer of ether. The brine solution is then run off as completely as possible and the ether layer is dehydrated over solid calcium chloride, decanted into a distilling flask containing a few pieces of sodium and finally distilled from the water bath, the receiver being cooled in ice-cold water.

Method (*ii*).—*Continuous ether process.*

  Required 70 c.c. concentrated sulphuric acid,
          100 c.c. rectified spirit or absolute alcohol.

Procedure.—The acid is slowly poured into the alcohol with constant shaking and cooling under the tap. The mixture is then transferred to a 500 c.c. distillation flask fitted with a double-bored cork carrying a dropping funnel and a thermometer, the bulb of which is completely immersed in the liquid. The side tube of the flask is connected to a

Liebig condenser, the other end of which is attached to an adapter and receiver cooled by ice and water. The flask is heated on a wire gauze or sand bath until the temperature reaches 140° C., when ether begins to distil over. At this point alcohol is allowed to drop from the funnel into the liquid at about the rate at which the liquid distils (about 3 drops a second). The temperature is kept at about 140° to 142° C. throughout the experiment. About 70 c.c. of distillate are collected; this contains water, alcohol, and sulphurous acid, in addition to ether.

The distillate is purified by shaking it with sodium hydroxide solution in a separating funnel to remove alcohol and sulphurous acid. It is allowed to stand and the lower aqueous layer is run off. The washing with alkali is then repeated. The ether is then dehydrated by adding solid calcium chloride, allowing to stand for half an hour and decanting the ether into a dry flask. The ether is finally distilled from the water bath. Further purification from water and alcohol is obtained by distillation in the presence of metallic sodium.

The formation of ether from alcohol takes place in two stages. (Williamson was the first to give this explanation.) When alcohol is heated with sulphuric acid it is converted into ethyl hydrogen sulphate:

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$$

This compound then reacts with alcohol, yielding ether and re-forming the acid:

$$C_2H_5 \overline{| HSO_4 + H |} O \cdot C_2H_5 = C_2H_5 \cdot O \cdot C_2H_5 + H_2SO_4$$
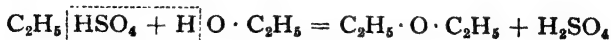
From these reactions it is clear that a given quantity of sulphuric acid is capable of converting a relatively large quantity of alcohol into ether. Practically, however, the acid becomes diluted and also diminished in volume by reduction to sulphurous acid; hence the process comes to an end after a period of time.

Manufacture of Ethyl Ether.—Ether is prepared on the large scale by boiling in a large lead-lined vessel A (fig. 24), at 140 to 145° C., a mixture of 5 parts of 96 per cent alcohol and 9 parts of concentrated sulphuric acid. The volume of liquid in A is kept unchanged by allowing alcohol to flow at a uniform rate from the tank B through a leaden pipe
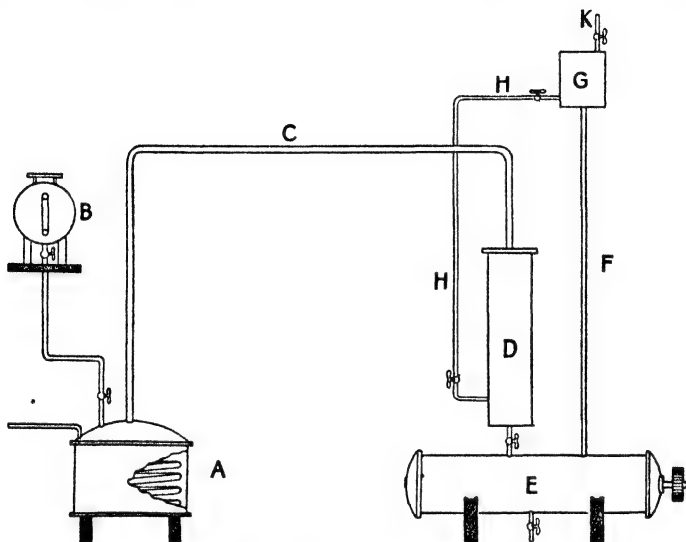
Fig. 24.—Plant for Manufacture of Ether

dipping into the boiling liquid, the rate being such that the volume of alcohol added is the same as the volume of liquid evaporated.

The ether which distils from A passes by means of the pipe C into the condenser D and runs into the cylindrical tank E, where it is agitated by stirrers with sodium carbonate or milk of lime, to remove any acid conveyed over from A. During the reaction between the acid and alcohol, permanent gases, e.g. ethylene, are formed, which escape through the tube F into the condenser G, where any ether vapour is condensed and returns to D and E by means

of the tube HH. The gases then escape into the air through K.

Commercial ether always contains sulphonic acids and esters which are formed by side reactions which take place simultaneously; hence the sulphuric acid which is continually regenerated diminishes in efficiency and must be renewed every month.

Pure ether is obtained by treating the commercial product with sodium, which destroys all water and alcohol, and then distilling.

Constitution of Ether.

The constitution of ether is derived from its formation from ethyl iodide and sodium ethoxide (Method (i), p. 141). This reaction may be structurally expressed as follows:

$$
\begin{array}{cccc}
\text{H} & \text{H} & & \text{H} \quad \text{H} \\
| & | & & | \quad | \\
\text{H—C—C—} & \boxed{\text{I} + \text{Na}} & \text{—O—C—C—H} \\
| & | & & | \quad | \\
\text{H} & \text{H} & & \text{H} \quad \text{H}
\end{array}
$$

$$
= \begin{array}{cccc}
\text{H} & \text{H} & \text{H} & \text{H} \\
| & | & | & | \\
\text{H—C—C—O—C—C—H} & + \text{NaI} \\
| & | & | & | \\
\text{H} & \text{H} & \text{H} & \text{H}
\end{array}
$$
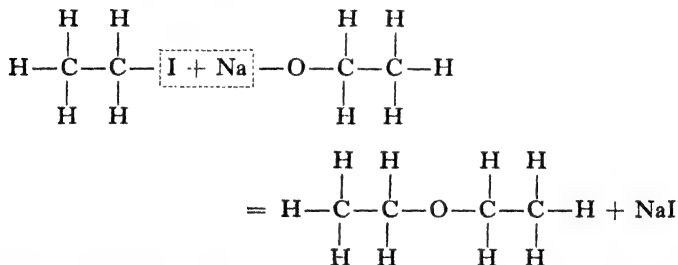
which indicates that two ethyl groups are linked together by means of an oxygen atom as in the alkali oxides, e.g. Na—O—Na. This structural formula is confirmed by a study of the chemical properties of ether. It contains no hydroxyl group, hence it does not react with an alkali metal or with phosphorus pentachloride. Williamson (1851) first synthesized ether by means of this reaction.

Properties of Ether.

It is a colourless, mobile, neutral, pleasant-smelling liquid of sp. gr. 0·736 at 0° C. It is very volatile and exceed-

ingly inflammable; its vapour is very heavy, and forms an explosive mixture with air or oxygen:

$$C_4H_{10}O + 6O_2 = 4CO_2 + 5H_2O$$
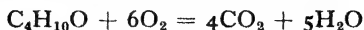
It boils at 35° C. and solidifies at −117·6° C.

Uses.—As an anæsthetic, either by inhalation or externally for producing local insensibility in minor operations. For refrigerating plant, owing to its abnormal lowering of temperature on evaporation. It is an excellent solvent for oils, fats, resins, alkaloids, &c., and is used as an extractive in organic chemistry, especially in the manufacture of dyestuffs and collodion.

Morton (1846) and Simpson (1848) were the first to introduce it into surgery.

C. Amines

Amines are compounds formed by the substitution or alkyl radicles for one or more hydrogen atoms in ammonia. They are also called *substituted* or *compound ammonias*, of *ammonia bases.* They closely resemble both ammonia and the alkalis, exhibiting a more strongly basic character than ammonia. They form one of the groups of organic bases.

The amines are subdivided into primary, secondary, and tertiary amines according to the number of hydrogen atoms in ammonia which have been replaced by alkyl radicles. The methyl derivatives have the following structural formulæ and names:

	Methylamine	Dimethylamine	Trimethylamine
	(Primary amine)	(Secondary amine)	(Tertiary amine)
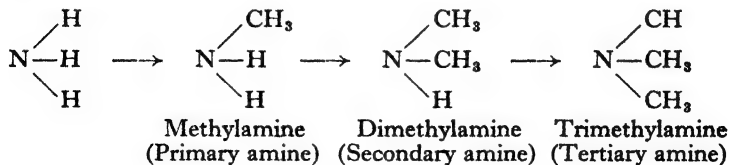
The primary amines contain the **Amino Group** $-NH_2$.
The secondary amines contain the **Imino Group** $=NH$.
The tertiary amines contain the **Nitrogen Atom** $\equiv N$.

Mixed amines can be formed by substituting different alkyl radicles for hydrogen atoms in ammonia, e.g.

$$\begin{matrix} CH_3 \diagdown \\ C_2H_5 \!-\! N, \text{ Methyl ethylamine} \\ H \diagup \end{matrix}$$
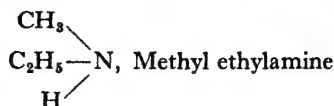
Methylamine, $CH_3 . NH_2$.

Occurrence.—In herring brine, pyroligneous acid, and the distillate from bones. It is also found in the decomposition products of certain organic compounds, especially the alkaloids.

Formation.—1. By boiling the methyl ester of cyanic acid (methyl isocyanate) with potassium hydroxide (Wurtz, 1849):

$$CH_3 \cdot N = \overline{\left| CO + KO \right|} H$$
$$KO \left| H = CH_3NH_2 + K_2CO_3; \right.$$

Methyl isocyanate

compare

$$H \cdot N = CO + 2KOH = H \cdot NH_2 + K_2CO_3.$$

Hydrogen isocyanate
(Cyanic acid)
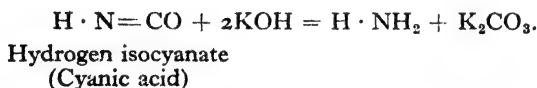
This reaction indicates that (*a*) methyl isocyanate does not behave as a true ester, since no alcohol is formed on hydrolysis; similarly for other esters of cyanic acid: (*b*) the alkyl group in isocyanates is in all probability attached to the nitrogen atom and not to the oxygen atom (cf. p. 343).

2. By heating methyl chloride, bromide, or iodide in closed vessels with alcoholic ammonia:

$$CH_3I + NH_3 = CH_3NH_2 \cdot HI$$
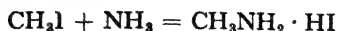
The halogen acid produced during the interaction combines with the amine to form a salt.

3. By acid reduction of nitro-methane (p. 159):

$$CH_3NO_2 + 3H_2 = CH_3NH_2 + 2H_2O$$

4. By the action of bromine and potassium hydroxide solution on amides (p. 205) of fatty acids (*Hofmann's method*). (The resulting amine has one carbon atom less than the amide used, e.g. acetamide gives methylamine.)

Equivalent amounts of acetamide and bromine are mixed and a 10 per cent solution of potash is added until the colour of the bromine disappears; acetobromamide is produced:

$$CH_3CONH_2 + Br_2 + KOH = CH_3CO \cdot NHBr + KBr + H_2O$$
Acetamide   Acetobromamide

The resulting solution is gently warmed with excess of potash, and methylamine is evolved:

$$CH_3CO \cdot NHBr + 3KOH = CH_3NH_2 + K_2CO_3 + KBr + H_2O$$

Note.—Intermediate products are formed during the reaction (p. 207).

5. By passing a mixture of an alcohol and ammonia over heated thoria (*Sabatier's method*).

$$CH_3OH + NH_3 = CH_3NH_2 + HOH$$

Properties.—A colourless gas with a strong ammoniacal fishy smell; differs from ammonia in being inflammable, burning with a lambent bluish flame. It condenses to a

liquid at $-6°$ C. It is soluble in water. Its chemical properties are similar to those of ammonia; e.g. it precipitates metallic hydroxides (but unlike ammonia, it does not redissolve cadmium, nickel, and cobalt hydroxides when added in excess). It neutralizes acids, forming salts which are readily soluble in water:

$CH_3NH_2 \cdot HCl$	$CH_3NH_2 \cdot HNO_3$	$(CH_3NH_2)_2 \cdot H_2SO_4$
Methylamine hydrochloride	Methylamine nitrate	Methylamine sulphate
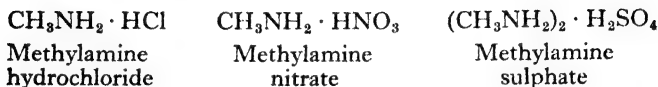
Methylamine in aqueous solution reacts with the chlorides of mercury, gold, and platinum to form double salts known as methylamine mercuri-, auri-, and platini-chlorides respectively.

$$(CH_3NH_3)_2PtCl_6 \text{ or } (CH_3NH_2 \cdot HCl)_2PtCl_4; \quad cf. (NH_4)_2PtCl_6$$

Methylamine platinichloride · · · · · · · · · · · · Ammonium platinichloride

$$(C_2H_5 \cdot NH_3)AuCl_4 \text{ or } (C_2H_5NH_2 \cdot HCl)AuCl_3$$
Ethylamine aurichloride
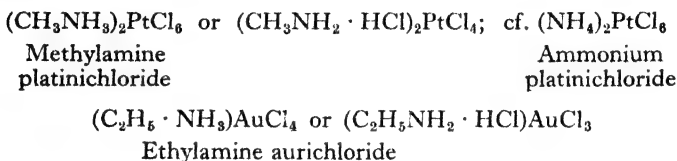
These salts are easily obtained by dissolving the amine in 50 per cent hydrochloric acid and adding the appropriate metallic chloride.

The platinichlorides are yellow crystalline substances analogous to ammonium platinichloride (chloroplatinate).

The formation of these double salts is a general reaction given by other amines.

Methylamine reacts with glycine (p. 251) to form methyl glycine (sarcosine):

$$CH_3NH_2 + CH_2NH_2COOH = CH_3NH \cdot CH_2COOH + NH_3$$

Sarcosine is obtained when naturally-occurring substances, e.g. creatine and caffeine, are decomposed (p. 252).

Dimethylamine, $(CH_3)_2NH$.

Occurrence.—In Peruvian guano and in pyroligneous acid.

Formation.—1. Special reaction: by treating dimethyl-aniline with nitrous acid:

Dimethylaniline   *p*-nitroso-dimethyl aniline
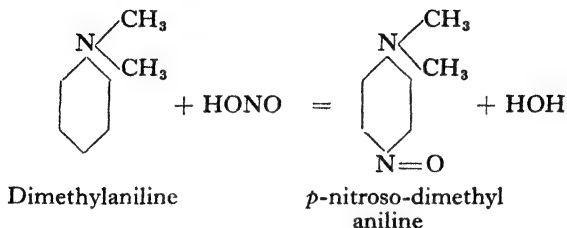
The nitroso-dimethylaniline, $(CH_3)_2N \cdot C_6H_4 \cdot NO$, obtained is then decomposed by sodium hydroxide:

Nitroso-dimethyl-aniline   Nitroso-phenol
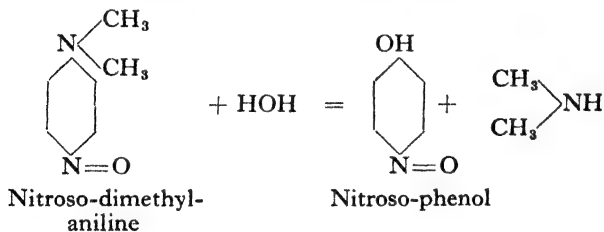
2. By the action of methyl iodide on the primary compound:
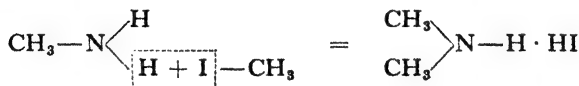
Dimethylamine is a gas (b. pt. $7°$ C.).

Trimethylamine, $(CH_3)_3N$.

Occurrence.—In herring brine, putrefied fish, certain plants, and the distillate from beet sugar molasses.

Formation.

1. *Commercial Method.*—It is obtained as a decomposition product from complicated organic compounds containing nitrogen, e.g. from the betaine of beetroot, and accordingly is produced along with ammonia, dimethylamine, methyl alcohol, acetonitrile, &c., by the distillation of vinasse (residues from beet sugar). The trimethylamine is collected as the hydrochloride $N(CH_3)_3 \cdot HCl$. Commercial " trimethylamine " contains 50 per cent dimethylamine, 5 per cent trimethylamine, and varying proportions of primary methyl-, ethyl-, propyl- and butyl-amines. It is used for the preparation of methyl chloride:

$$(CH_3)_3N \cdot HCl + 3HCl = 3CH_3Cl + NH_4Cl$$

2. By heating formalin (p. 164) with ammonium chloride in an autoclave to $110°$ C.

$$9HCHO + 2NH_3 = 2N(CH_3)_3 + 3CO_2 + 3H_2O$$
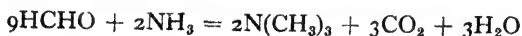
Properties.—Trimethylamine is a colourless gas with a strong ammoniacal and fishy odour. It condenses to a liquid at $3·5°$ C. It is very stable in water and alcohol and is a strong base. Like other tertiary amines, it unites with a molecule of alkyl iodide to form quaternary ammonium iodide (cf. NH_4I):

$$(CH_3)_3N + CH_3I = N(CH_3)_4I$$

Characteristic and Distinguishing Tests of Primary, Secondary and Tertiary Amines

I. *Primary Amines* when treated with nitrous acid in aqueous solution yield the **alcohol** and **nitrogen**:

$$\begin{array}{c|c|c} CH_3 & N & H_2 \\ & + & \\ HO & N & O \end{array} = CH_3OH + N_2 + H_2O$$
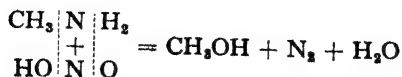
This reaction is similar to the action of nitrous acid on ammonia:

$$H | N | H_2$$
$$| + |$$
$$HO | N | O = N_2 + 2H_2O$$
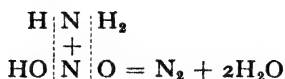
Experiment.—Pour 20 c.c. of trimethylamine solution into a small flask fitted with a delivery tube, then add 10 c.c. of dilute hydrochloric acid and about 2 gm. of sodium nitrite. Warm the mixture very gently; effervescence begins and the nitrogen evolved can be collected. Test for methyl alcohol in the flask (pp. 526, 537).

Secondary Amines when treated with nitrous acid give no effervescence, but a yellow oil, called a **nitrosamine,** separates, which is volatile in steam. All nitrosamines give Liebermann's reaction with phenol (see pp. 456, 535).

$$(CH_3)_2N \boxed{H + HO} \cdot NO = (CH_3)_2N \cdot NO + H_2O$$
$$\text{Dimethyl nitrosamine}$$
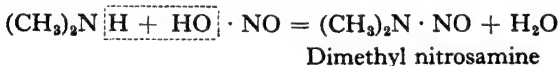
Tertiary Amines give no reaction with nitrous acid.

II. Primary Amines give the **carbylamine** or **iso-cyanide** reaction. Methylamine with chloroform and alcoholic potash forms methyl isocyanide, which has an intolerable smell (cf. pp. 97, 449):

$$CH_3NH_2 + CHCl_3 + 3KOH = CH_3 \cdot N \cdot C + 3KCl + 3H_2O$$

Secondary and Tertiary Amines do not form isocyanides.

III. *Primary and Secondary Amines* combine with acid chlorides and anhydrides to form **amides.**

$$CH_3CO \cdot Cl + CH_3NH_2 = CH_3CO \cdot NH \cdot CH_3 + HCl$$
$$\text{Methyl acetamide}$$
$$CH_3CO \cdot Cl + (CH_3)_2NH = CH_3CO \cdot N(CH_3)_2 + HCl$$
$$\text{Dimethyl acetamide}$$
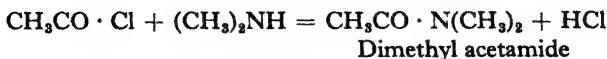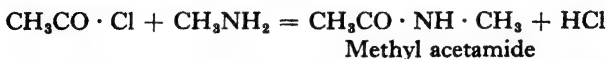
Tertiary Amines do not give these reactions.

IV. *Primary and Secondary Amines*, but not Tertiary Amines, react with ethyl oxalate to form a solid amide and a liquid oxamic ester respectively (*Hofmann's method of separation*, p. 156):

$$CO \cdot \boxed{OC_2H_5 \quad H} \cdot NH \cdot CH_3 \qquad CO \cdot NH \cdot CH_3$$
$$| \qquad\qquad + \qquad = \quad | \qquad\qquad\quad + 2C_2H_5OH$$
$$CO \cdot \boxed{OC_2H_5 \quad H} \cdot NH \cdot CH_3 \qquad CO \cdot NH \cdot CH_3$$

Dimethyl oxamide
(a solid)

$$CO \cdot \boxed{OC_2H_5} \qquad\qquad\qquad CO \cdot N(CH_3)_2$$
$$| \qquad\qquad\quad + H \cdot N \cdot (CH_3)_2 \; = \; | \qquad\qquad + C_2H_5OH$$
$$CO \cdot OC_2H_5 \qquad\qquad\qquad\quad COOC_2H_5$$

Dimethyl oxamic ester
(a liquid)
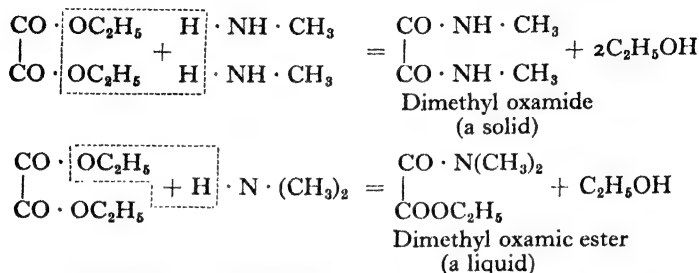
V. Hinsberg's Reagent (Benzene sulphonic chloride, $C_6H_5SO_2Cl$).

Primary Amines unite with this reagent to form compounds which contain an acidic —NH group and are *soluble* in sodium hydroxide or potash.

Benzene sulphonic   Methyl benzene
chloride   sulphonamide
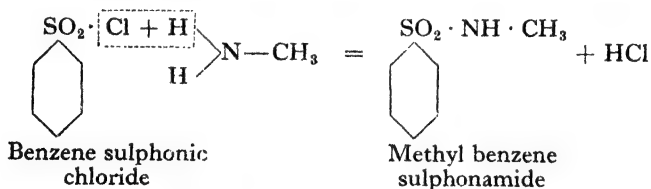
Secondary Amines unite with this reagent to form compounds *insoluble* in sodium hydroxide or potash (indicating the absence of acidic —NH group).

Dimethyl benzene
sulphonamide
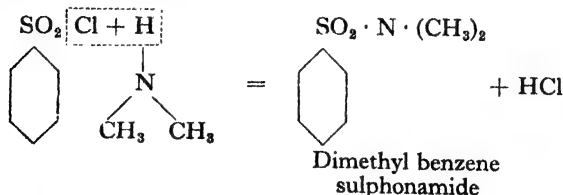
Tertiary Amines do not react with this reagent.

VI. *Tertiary Amines* combine with alkyl halides to form **quaternary ammonium halides:**

$$\begin{matrix} CH_3 \\ \diagdown \\ CH_3{-}N \\ \diagup \\ CH_3 \end{matrix} + CH_3I = \begin{matrix} CH_3 \\ \diagdown \diagup CH_3 \\ CH_3{-}N \\ \diagup \diagdown I \\ CH_3 \end{matrix} \quad \text{or} \quad N(CH_3)_4I \quad \text{(cf. } NH_4I)$$
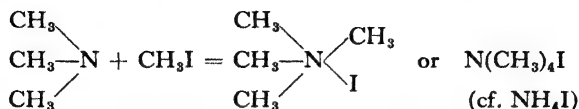
Primary and Secondary Amines do not form these compounds.

The quaternary compounds may be regarded as ammonium salts in which the four hydrogen atoms of the $NH_4{-}$ group have been replaced by organic radicles. They react with moist silver oxide to produce quaternary ammonium hydroxides:

$$\begin{matrix} CH_3 \\ \diagdown \diagup CH_3 \\ CH_3{-}N \\ \diagup \diagdown \overline{I + Ag} \, OH \\ CH_3 \end{matrix} = \begin{matrix} CH_3 \\ \diagdown \diagup CH_3 \\ CH_3{-}N \\ \diagup \diagdown OH \\ CH_3 \end{matrix} + AgI, \text{ or } N(CH_3)_4OH \quad \text{(cf. } NH_4OH)$$

Tetramethyl ammonium
hydroxide
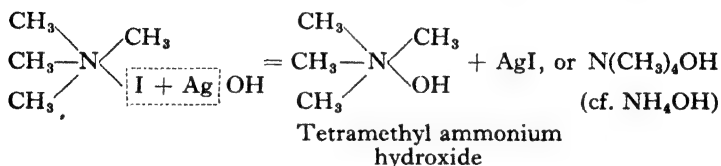
Tetramethyl ammonium hydroxide is a white deliquescent crystalline solid.

Quaternary hydroxides decompose in two ways:

A. Those which have only one carbon atom in the radicles form an alcohol and a tertiary amine:

$$(CH_3)_4N \cdot OH = (CH_3)_3N + CH_3OH$$
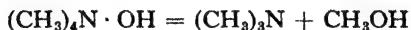
B. Those which have two or more carbon atoms in a radicle form a tertiary amine and an olefine:

$$\begin{matrix} (CH_3)_3 \\ \diagdown \\ C_2H_5 \diagup \end{matrix} N \cdot OH = (CH_3)_3N + C_2H_4 + H_2O$$
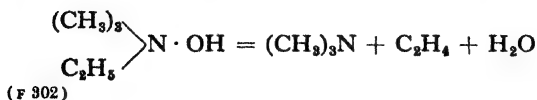
The primary, secondary and tertiary bases are derived from ammonia, whilst the quaternary bases are derived from the hypothetical ammonium hydroxide. The strength of these bases increases with the increase in the number of alkyl groups. The quaternary ammonium hydroxides are strong bases and resemble the alkali hydroxides.

Like ammonia, these bases precipitate hydroxides from solutions of metallic salts, but frequently redissolve the precipitated hydroxides.

Methylamine, however, does not dissolve $Ni(OH)_2$ and $Co(OH)_2$, i.e. it differs from ammonia in this respect.

Ethylamine dissolves $Al(OH)_3$ and also $Cu(OH)_2$ with difficulty; but does not dissolve $Fe(OH)_3$ and $Cd(OH)_2$.

Methyl iodide acts on these bases and on ammonia as follows:

$$NH_3 + CH_3I = CH_3NH_2 \cdot HI \quad \text{Methylamine hydriodide}$$
$$CH_3NH_2 + CH_3I = (CH_3)_2NH \cdot HI \quad \text{Dimethylamine hydriodide}$$
$$(CH_3)_2NH + CH_3I = (CH_3)_3N \cdot HI \quad \text{Trimethylamine hydriodide}$$
$$(CH_3)_3N + CH_3I = (CH_3)_4N \cdot I \quad \text{Tetramethyl ammonium iodide}$$
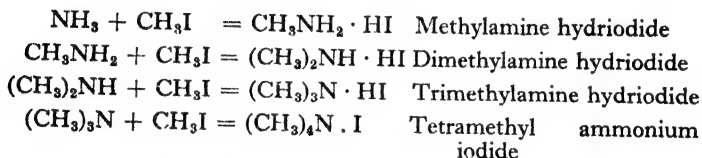
The **ethylamines** can be prepared by methods similar to those described under the methylamines.

Ethylamine, $C_2H_5NH_2$.

Formation.—1. By boiling ethyl isocyanate with potassium hydroxide.

2. By heating ethyl chloride with alcoholic ammonia.

3. By reduction of nitro-ethane (p. 159) or acetonitrile (p. 339).

4. By Hofmann's method, using propionamide.

For Practice.—Write down equations for the above reactions.

Properties.—Ethylamine is a colourless, volatile liquid

(b. pt. 19° C.). It has a strong ammoniacal smell and biting taste. It burns with a yellow flame and is very soluble in water.

Diethylamine, $(C_2H_5)_2NH$.

Formation.—1. By the action of the alkyl halide on the primary compound (general method):

$$C_2H_5NH_2 + C_2H_5I = (C_2H_5)_2NH + HI$$

2. By the action of the alkyl hydrogen sulphate on the primary compound (general method):

$$C_2H_5NH_2 + C_2H_5HSO_4 = (C_2H_5)_2NH + H_2SO_4$$
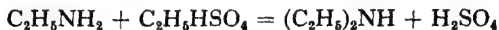
It is a colourless liquid with a strong fishy smell (b. pt. 56° C.).

Triethylamine, $(C_2H_5)_3N$.

It is prepared by heating the alkyl halide with the secondary compound (general method):

$$(C_2H_5)_2NH + C_2H_5I = (C_2H_5)_3N + HI$$
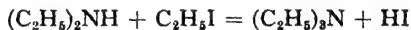
It is an oily, strongly alkaline liquid with a strong fishy smell (b. pt. 90° C.).

Separation of the Amines

1. Hinsberg's Method (p. 152).

After treatment with benzene sulphonic chloride followed with caustic alkali, the mixture is treated with ether. The ether dissolves the tertiary amine and the secondary compound, e.g. $C_6H_5SO_2N(CH_3)_2$, but not the primary compound, which remains dissolved in the aqueous alkaline solution. The ethereal layer is removed.

A. The aqueous solution is then treated with concentrated hydrochloric acid; the primary amine is regenerated in the form of its salt, e.g.:

$$C_6H_5SO_2NHCH_3 + 2HCl = C_6H_5SO_2Cl + CH_3NH_2 \cdot HCl$$
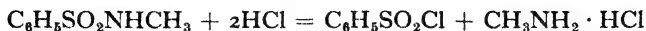
By heating this salt with a caustic alkali the primary amine is regenerated and can be distilled over, or, if a gas, collected in water or other solvent.

B. The ethereal layer is distilled: the ether and the tertiary amine distil over; if the tertiary amine is a gas, it is collected in water and so separated from the ether.

The secondary amine compound, $C_6H_5SO_2N(CH_3)_2$, remains in the distilling flask and is treated in the same way as the primary compound (A).

Note.—This was Hinsberg's original method; to meet criticism he amended it, using instead of benzene sulphonic chloride the compound β-anthraquinone sulphonic chloride. The amended method is similar in principle, the secondary and tertiary compounds being soluble in ether, whilst the primary is insoluble.

2. **Hofmann's Method** (p. 152).

Caustic potash is added to the three classes of amines or their salts, and the quaternary compound, and the mixture distilled. The primary, secondary, and tertiary amines distil over, leaving the non-volatile quaternary ammonium compound in the distilling flask. Ethyl oxalate is then added to the distillate, after the latter has been freed from water. If the amines are gases, they are passed into ethyl oxalate solution. The primary amine forms a solid amide, the secondary amine a liquid oxamic ester, whilst the tertiary amine is not acted upon. On distilling this mixture, the tertiary amine distils over, as it has the lowest boiling point. The solid amide is then filtered off from the liquid oxamic ester. These compounds are then separately decomposed

and distilled, and the primary and secondary amines are obtained:

$$
\begin{array}{l}
\overset{\displaystyle CH_3}{\underset{\displaystyle}{|}} \\
CO \cdot NH + H \,OK \\
| \\
CO \cdot NH + H \,OK \\
| \\
CH_3
\end{array}
= 2CH_3NH_2 + \begin{array}{l} COOK \\ | \\ COOK \end{array}
$$

Dimethyl oxamide   Methyl-   Potassium
                        amine   oxalate

$$
\begin{array}{l}
(CH_3)_2 \\
| \\
CO \cdot N \quad + H \,OK \\
| \\
CO \cdot O\,C_2H_5 + HO\,K
\end{array}
= (CH_3)_2NH + C_2H_5OH + \begin{array}{l} COOK \\ | \\ COOK \end{array}
$$

Dimethyl oxamic   Dimethyl-   Ethyl   Potassium
       ester   amine   alcohol   oxalate
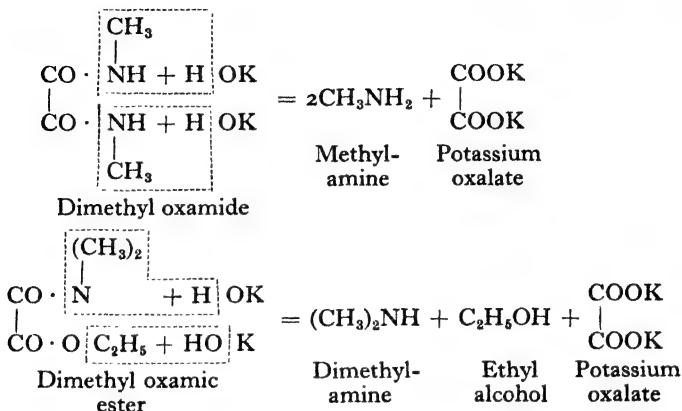
BOILING-POINTS OF THE LOWER AMINES

	Primary	Secondary	Tertiary
Methylamine	$-6°$ C.	$7°$	$3·5°$
Ethylamine	$+19°$	$56°$	$90°$
n-propylamine	$49°$	$110°$	$156°$
n-butylamine	$76°$	$160°$	$215°$

Ascent and Descent of a Homologous Series

Various reactions given above enable us to convert methyl alcohol into ethyl alcohol and vice versa; similarly, other alcohols can be converted into the next higher or lower homologue. This process is also referred to as " passing up " or " passing down " the homologous series.

Ascent

$$
\underset{\substack{\text{Methyl}\\\text{alcohol}}}{CH_3OH} \xrightarrow{\text{(HI)}} \underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3I} \xrightarrow{\text{(KCN)}} \underset{\substack{\text{Methyl}\\\text{cyanide}}}{CH_3CN} \xrightarrow{\text{(H)}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{\text{(HNO}_2)} \underset{\text{Ethyl alcohol}}{C_2H_5OH}
$$

Descent

$$\overset{\text{(O)}}{} \qquad \overset{\text{(NH}_3)}{} \qquad \overset{\text{(Br + KOH)}}{} \qquad \overset{\text{(HNO}_2)}{}$$

$$C_2H_5OH \rightarrow CH_3COOH \dashrightarrow CH_3CONH_2 \dashrightarrow CH_3NH_2 \dashrightarrow CH_3OH$$

Ethyl   Acetic acid   Acetamide   Methylamine   Methyl
alcohol   alcohol
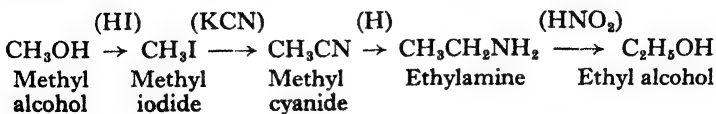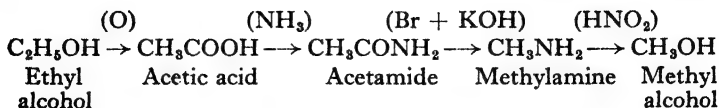
Again, it is possible to convert a higher fatty acid into its next higher or lower homologue.

Ascent

$$\overset{\text{(Ca salt)}}{} \qquad \overset{\text{(H)}}{} \qquad \overset{\text{(HI)}}{} \qquad \overset{\text{(KCN)}}{}$$

$$CH_3COOH \longrightarrow CH_3CHO \dashrightarrow CH_3CH_2OH \longrightarrow CH_3CH_2I \longrightarrow$$

Acetic acid   Acetaldehyde   Ethyl   Ethyl
                                   alcohol   iodide

$$\overset{\text{(Hydrolysis)}}{}$$

$$CH_3CH_2CN \longrightarrow CH_3CH_2COOH.$$

Ethyl   Propionic
cyanide   acid
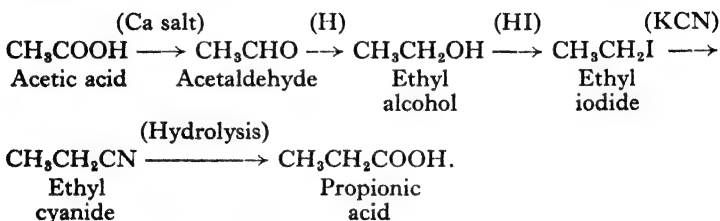
The ethyl cyanide may also be converted as follows:

$$\overset{\text{(H)}}{} \qquad \overset{\text{(HNO}_2)}{} \qquad \overset{\text{(O)}}{}$$

$$CH_3CH_2CN \rightarrow CH_3CH_2CH_2NH_2 \longrightarrow CH_3CH_2CH_2OH \dashrightarrow$$

Ethyl cyanide   Propylamine   Propyl alcohol

$$\overset{\text{(O)}}{}$$

$$CH_3CH_2CHO \dashrightarrow CH_3CH_2COOH.$$

Propaldehyde   Propionic acid

Descent

$$\overset{\text{(NH}_3)}{} \qquad \overset{\text{(Distil)}}{} \qquad \overset{\text{(Br + KOH)}}{}$$

$$CH_3COOH \longrightarrow CH_3COONH_4 \longrightarrow CH_3CONH_2 \longrightarrow CH_3NH_2$$

Acetic acid   Ammonium   Acetamide   Methylamine
                acetate

$$\overset{\text{(HNO}_2)}{} \qquad \overset{\text{(O)}}{} \qquad \overset{\text{(O)}}{}$$

$$\longrightarrow CH_3OH \longrightarrow HCHO \longrightarrow HCOOH.$$

Methyl   Formaldehyde   Formic
alcohol   acid
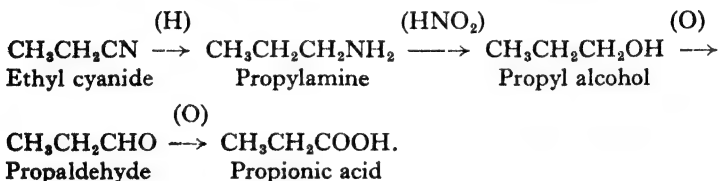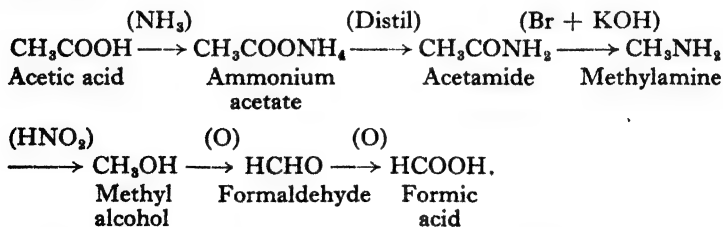
These reactions are general and should be carefully studied.

D. NITRO-PARAFFINS

Nitrous acid forms *two* types of isomeric compounds of the general formula $C_nH_{2n+1}NO_2$, known respectively as alkyl nitrites and nitro-paraffins. The nitrites are regarded as the true esters of nitrous acid. A comparison between these compounds is given below.

Alkyl Nitrites	Nitro-paraffins
Formation. By the action of nitrous acid on the alcohol: $C_2H_5OH + HNO_2 = C_2H_5NO_2 + H_2O$	*Formation.* By distilling solid silver nitrite with the alkyl iodide: $C_2H_5I + AgNO_2 = C_2H_5NO_2 + AgI$
Properties. Mainly neutral liquids, aromatic odour, insoluble in water. Lower boiling-points, e.g.: Methyl nitrite, b. pt. $-12°$ C. Ethyl nitrite, b. pt. $+18°$ C.	*Properties.* Colourless liquids, ethereal odour, insoluble in water. Higher boiling-points, e.g.: Nitro-methane, b. pt. $100°$ C. Nitro-ethane, b. pt. $113.5°$ C.
Reactions. 1. With caustic alkalis hydrolysis takes place, e.g.: $C_2H_5NO_2 + KOH = C_2H_5OH + KNO_2$ Ethyl nitrite	*Reactions.* 1. A potassium derivative is formed: $C_2H_5NO_2 + KOH = C_2H_4KNO_2 + H_2O$ Nitro-ethane Potassium nitro-ethane
2. On reduction: an alcohol and hydroxylamine or ammonia are formed: $C_2H_5NO_2 + 2H_2 = C_2H_5OH + NH_2OH$ $C_2H_5NO_2 + 3H_2 = C_2H_5OH + NH_3 + H_2O$	2. On reduction: amines are formed: $C_2H_5NO_2 + 3H_2 = C_2H_5NH_2 + 2H_2O$ This reaction shows that the nitrogen atom is directly linked to a carbon atom.
3. Vapour mixed with hydrogen and passed over finely divided nickel: an amine is formed.	3. Similar to the nitrite.
Structure: Ethyl nitrite:	*Structure:* Nitro-ethane:
Nitrogen atom not directly linked to a C atom; proved by the fact that they are easily hydrolysed and reduced.	Nitrogen atom directly linked to a C atom; proved by the facts that they are difficult to hydrolyse and that amines are formed.

QUESTIONS

1. Give a concise but careful account of Hofmann's work on the preparation and separation of the amines.

2. Describe with essential practical details how you would prepare ethyl acetate on a comparatively small scale. Write equations representing the formation of the products obtained from it by interaction with (*a*) sodium hydroxide, (*b*) ammonia.
(*Chemists and Druggists Qual.*)

3. Give a method for distinguishing between primary, secondary and tertiary amines. How would you obtain pure di-ethylamine from a mixture of mono-ethylamine and di-ethylamine? (*Phar. Chem. Qual.*)

4. If you were given an amine, how would you determine its molecular weight and ascertain whether it was primary, secondary or tertiary?

5. Describe carefully, giving practical details, how you would prepare aceto-acetic ester from ethyl acetate. Explain and illustrate its importance as the starting point in the synthesis of other compounds. (*Phar. Chem. Qual.*)

6. Compare and contrast the properties and reactions of alcohols and ethers.
With what groups of inorganic compounds may these groups of organic substances be compared?

7. How would you effect the following transformations:

(*a*) ethylene into acetylene;
(*b*) ethylene into ethyl bromide;
(*c*) ethyl iodide into acetic acid;
(*d*) ethylamine into ethyl alcohol;
(*e*) nitro-ethane into ethylamine.

(*Chemists and Druggists Qual.*)

8. Give the names and structural formulæ in each case of the two compounds possessing the molecular formula: (*a*) C_4H_{10}, (*b*) C_2H_6O, (*c*) C_3H_8O, (*d*) C_3H_6O.

9. By reference to examples indicate the products of oxidation of primary and secondary alcohols.

By what methods may ethyl alcohol be converted into ethyl acetate?

10. Give an account of the commercial method for the preparation of methyl alcohol.

Describe how you would prepare in the laboratory from methyl alcohol a pure specimen of either (*a*) methyl iodide, or (*b*) methyl acetate. (*Higher School Cert.*)

11. Give an account of the evidence on which the accepted constitution of ethyl alcohol *or* ethyl ether is based.

12. Describe the preparation of pure ethyl hydrogen sulphate. How could you obtain from this substance (*a*) diethyl ether, (*b*) methyl ethyl ether?

13. Describe briefly how the following substances may be prepared from ethyl alcohol: (*a*) ethyl iodide, (*b*) ethyl acetate, (*c*) acetaldehyde, (*d*) ethylene. Explain in each case the reactions involved. (*I. M.B., London.*)

14. How does potassium hydroxide react with the following compounds: carbon monoxide, chloroform, carbon tetrachloride, ethyl chloride, acetamide, chloral hydrate?

In each case mention the conditions under which the reaction proceeds most easily. (*Cambridge Higher School Cert.*)

15. Describe carefully how you would prepare from alcohol and purify (*a*) ethylene, (*b*) ether. Mention *one* chemical reaction whereby ethylene may be distinguished from ethane, and *one* whereby ether may be distinguished from an ester.

(*Oxford Higher School Cert.*)

16. Show how (*a*) propyl alcohol may be converted into ethyl alcohol, (*b*) how butyric acid, C_3H_7COOH, may be converted into propionic acid, C_2H_5COOH, and then into acetic acid CH_3COOH.

CHAPTER VI

Aldehydes

The name aldehyde is derived from a contraction of

Alcohol (AL) and Dehydrogenatum (DEHYD),

for aldehyde is formed when alcohol is deprived of hydrogen by the oxidation process.

The aldehydes form a homologous series of general formula:

$$C_nH_{2n}O \text{ or } C_nH_{2n+1}CHO$$

The various aldehydes are named from the acids produced when they are oxidized, e.g. HCHO, Formaldehyde, CH_3CHO, Acetaldehyde, &c.

The lower members are *neutral liquids* of peculiar smell, readily soluble in water, and volatile. Increase of carbon atoms leads to less soluble compounds, whilst the highest members are *solid* and odourless and only capable of being distilled under reduced pressure.

Formaldehyde, Methaldehyde, HCHO.

Probably occurs naturally in those plant cells which contain the green colouring matter chlorophyll (p. 372).

Formation.—1. By the dry distillation of calcium formate:

$$\begin{matrix} HCOO \\ HCOO \end{matrix} \Big\rangle Ca = HCHO + CaCO_3$$

162
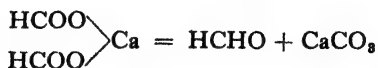
2. By passing a stream of air saturated with the vapour of methyl alcohol through a tube containing a copper spiral or platinized asbestos heated to dull redness:

$$CH_3OH + O = HCHO + H_2O$$

Experiment.—Pour 25 c.c. of methyl alcohol into a small beaker and suspend a red-hot platinum spiral just above the surface of the alcohol. The platinum wire continues to glow, owing to the oxidation of the alcohol, and the suffocating smell of formaldehyde is soon noticed.

Note.—Since formaldehyde is a gas, it is collected in solution, water being used as the solvent.

Properties.

Formaldehyde is a gas at ordinary temperatures, but when cooled it condenses to a liquid, boiling at $-21°$ C. Even at this low temperature polymerization takes place and trioxymethylene, $(CH_2O)_3$, is formed, and at ordinary temperatures this occurs with rapidity and with development of heat. Formaldehyde dissolves in water to the extent of 30 to 40 per cent; the solution has a very penetrating suffocating odour and a neutral reaction. On evaporating the aqueous solution on a water bath a white solid, *paraformaldehyde*, $(CH_2O)_{2 \text{ or } n}$ remains, which is soluble in water.

Formaldehyde in aqueous solution acts as a *reducing agent*, being oxidized to formic acid:

$$HCHO + O = HCOOH$$
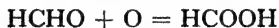
It reduces an ammoniacal solution of silver hydroxide (Tollen's reagent, p. 526), forming a silver mirror:

$$HCHO + Ag_2O = HCOOH + 2Ag$$

It also reduces mercuric chloride to mercurous chloride and then to mercury.

Uses.—As a strong antiseptic and disinfectant, especially for rooms; these are fumigated by the vapours evolved when a strong solution of formaldehyde or the solid *paraform* is heated. The *formalin* of commerce is a strong solution containing 40 per cent of formaldehyde dissolved in water. Paraform is the name given to solid paraformaldehyde (see below).

It is also used as a preservative for gums, glues, and starch solutions, and for preserving raw products in soap works, tanneries, &c. It is used in photography to render gelatine insoluble, in waterproofing with egg albumin, and in the manufacture of indigo and certain acridine dyestuffs.

When boiled with phenols, condensation takes place and resinous substances are formed which are used in the manufacture of ebonite, varnishes and *bakelite*. Bakelite is a very hard non-elastic substance used as a thermal and electrical insulator. Formaldehyde is also used in the after-treatment of direct cotton dyes and by gardeners to protect plants from parasites.

Formaldehyde readily changes either spontaneously or when heated into new compounds which can be reconverted into formaldehyde by simple means. This phenomenon is known as *polymerization* (see p. 81).

The Polymers of formaldehyde are:

(*a*) **Paraformaldehyde,** $(CH_2O)_{2 \text{ or } n}$, a white crystalline solid soluble in water.

(*b*) **Trioxymethylene,** $(CH_2O)_3$, a crystalline compound which passes into formaldehyde again when volatilized.

(*c*) **Formose,** $(CH_2O)_6$, a mixture of sugars produced by the action of lime-water or magnesia on a solution of formaldehyde. When the solution is filtered and the filtrate slowly evaporated, preferably under reduced pressure, a sweet syrupy solution remains, which has properties

somewhat similar to those of grape and fruit sugars (Chap. XIV).

$$6HCHO \quad = \quad C_6H_{12}O_6$$

Formaldehyde   Grape sugar
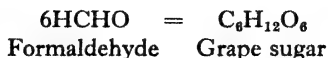
This suggests a mechanism for the production of sugar and starch from carbon dioxide in plants in the presence of chlorophyll (p. 372).

With potassium hydroxide, formaldehyde does not form a resin (p. 172), but is converted into methyl alcohol and formic acid. Formaldehyde reacts with ammonia to form a crystalline compound of the formula $(CH_2)_6N_4$ or *hexamethylene tetramine*, which is used in pharmacy under the name of *hexamine*:

$$6HCHO + 4NH_3 = (CH_2)_6N_4 + 6H_2O$$

Hexamine is used as a urinary disinfectant under the name of *urotropine*. These names are synonymous.

This reaction differs from that given by ammonia with acetaldehyde and other homologues of formaldehyde.

Formaldehyde reacts directly with sodium bisulphite and hydroxylamine as follows:

$$\begin{matrix} H \\ \\ H \end{matrix} \Big\rangle C{=}O + NaHSO_3 \quad = \quad \begin{matrix} H \\ \\ H \end{matrix} \Big\rangle C\Big\langle \begin{matrix} OH \\ \\ OSO_2Na \end{matrix}$$

Formaldehyde
sodium bisulphite

$$\begin{matrix} H \\ \\ H \end{matrix} \Big\rangle C{=}\overline{|O + H_2|}N \cdot OH = \begin{matrix} H \\ \\ H \end{matrix} \Big\rangle C{=}NOH + H_2O$$

Hydroxylamine   Formaldoxime
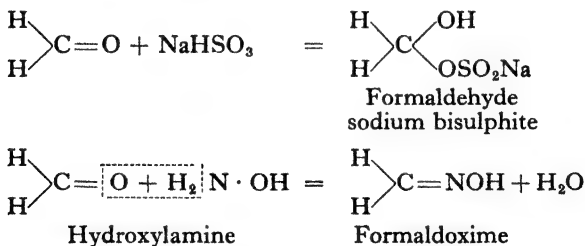
Methylal, $CH_2(OCH_3)_2$, is an important derivative of formaldehyde.

Formation.—1. By boiling an aqueous solution of formaldehyde with methyl alcohol and a small quantity of sulphuric acid.

2. By oxidizing methyl alcohol with manganese dioxide and sulphuric acid. The formaldehyde first produced reacts with the unchanged alcohol:

$$CH_3O \begin{array}{|c|} \hline H \\ \hline H \\ \hline \end{array} + O \begin{array}{|c|} \hline HCH \\ \hline \end{array} = H \cdot CH \begin{array}{c} OCH_3 \\ OCH_3 \end{array} + H_2O$$

Methyl   Formal-   Methylal
alcohol   dehyde
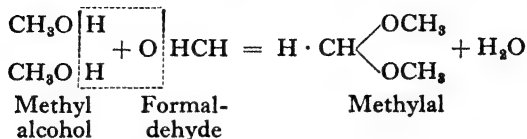
Methylal is a pleasant-smelling liquid (b. pt. 42° C.), readily soluble in water, and is used in medicine as a soporific.

Tests for Formaldehyde are given in Chap. XXII, p. 527. For use of formaldehyde in analysis, see Chap. XXVII, p. 615.

Acetaldehyde, Ethaldehyde, CH_3CHO.

Occurs in the " first runnings " in the rectification of refined spirit, having been formed by the oxidation of alcohol during the process of filtration through charcoal.

Formation.

1. By the dry distillation of a dry mixture of calcium acetate and calcium formate:

$$(CH_3COO)_2Ca + (HCOO)_2Ca = 2CH_3CHO + 2CaCO_3$$
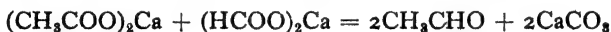
2. By the regulated oxidation of ethyl alcohol (i.e. a primary alcohol) either by

(*a*) potassium or sodium dichromate and H_2SO_4, or

(*b*) atmospheric oxygen and platinum, or

(*c*) potassium permanganate or manganese dioxide and H_2SO_4:

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O,$$
$$CH_3CH_2OH + O = CH_3CHO + H_2O.$$

The complete reaction is represented as follows:

$$3C_2H_5OH + K_2Cr_2O_7 + 4H_2SO_4$$
$$= K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3CH_3CHO$$
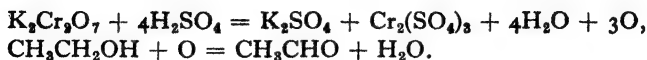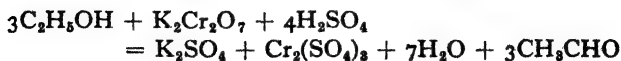
Experiment.—A mixture containing 120 gm. of concentrated sulphuric acid and 200 gm. of water is placed in a round-bottomed flask of capacity 1½ litres, fitted with a cork carrying a dropping funnel and a delivery tube connected with a long condenser. The end of the condenser is fitted with an adapter which leads into a receiver surrounded by a freezing mixture of ice and salt. When the contents of the flask have been heated on a sand bath just to boiling point, a mixture of a solution of 200 gm. each of sodium dichromate and water and 120 gm. of alcohol is added gradually through the tap funnel at the rate of one drop per second. The heat developed by the reaction is usually sufficient to keep the liquid boiling; if not, heat gently with caution. Aldehyde, water, alcohol, and acetal collect in the receiver. When all the dichromate mixture has been added heat for another 10 minutes.

Test the distillate with (*a*) Schiff's reagent, a solution of magenta decolorized by sulphur dioxide, (*b*) Tollen's reagent, (*c*) caustic soda solution.

3. From dihalogen substitution products containing the group —$CHCl_2$, by superheating with water or by boiling with water and lead oxide:

$$CH_3\text{——}\underset{\underset{Cl\quad\quad H}{|}}{\overset{\overset{Cl\quad\quad H}{|}}{C}}\text{——}H + O = CH_3CHO + 2HCl$$

Ethylidene dichloride
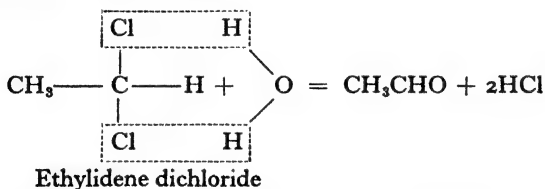
4. From acetyl chloride (p. 210) by dissolving it in moist ether and treating with sodium:

$$CH_3C\overset{O}{\underset{Cl}{\diagup}} + H\text{:}H = CH_3CHO + HCl$$
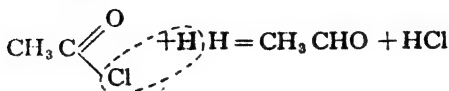
5. *Commercial Method.*—By passing acetylene into 30 per cent sulphuric acid at 80° C., using mercuric sulphate as a

catalyst. On addition of water to the alkyl hydrogen sulphate formed as an intermediate product, hydrolysis takes place and acetaldehyde is formed:

$$\begin{matrix} CH \\ ||| \\ CH \end{matrix} + \begin{matrix} H_2 \\ || \\ O \end{matrix} = \begin{matrix} CH_3 \\ | \\ CHO \end{matrix}$$

WATER AT 35°C

ALDEHYDE
ALCOHOL
AND WATER

ETHER
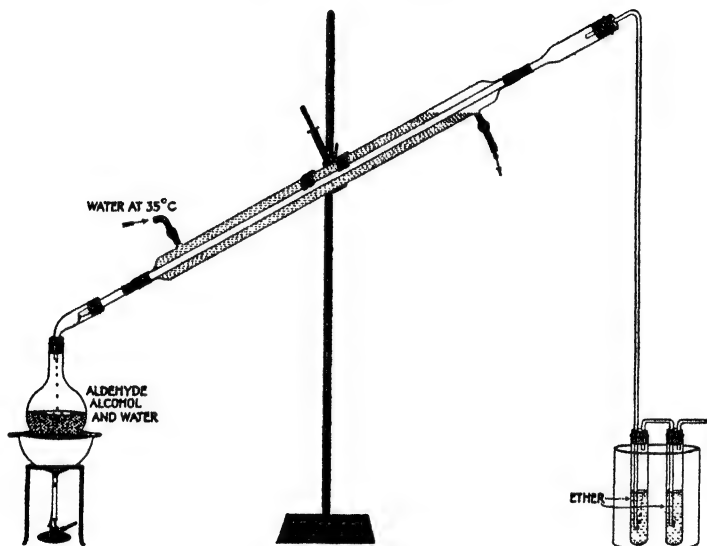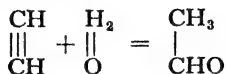
Fig. 25.—Preparation of Acetaldehyde-ammonia

Purification of Acetaldehyde.

The aldehyde cannot be separated by fractional distillation, so the impure acetaldehyde is treated in the following manner:

The distillate is transferred to a flask (fig. 25) placed on a water-bath and connected by means of an adapter to a Liebig condenser. This condenser is placed in an inclined position and serves as a semi-reflux. Water is admitted into the outer jacket of the condenser at a temperature of 30 to 35° C. The mouth of the condenser is joined by a long

vertical tube to two narrow absorption vessels of capacity about 100 c.c.; these contain about 40 c.c. each of dry ether and are cooled by ice.

The contents of the flask are gently heated to boiling. The alcohol and aqueous vapours condense in the condenser tube and return to the flask, while the acetaldehyde, which has a boiling point of 20·8° C., passes over and readily dissolves in the ether. After half an hour's heating, the absorption vessels are disconnected from the condenser and dry ammonia gas is slowly passed through the ethereal solution until it is saturated, when the whole of the aldehyde separates out in the form of colourless crystals of aldehyde-ammonia:

$$CH_3CHO + NH_3 = CH_3 \cdot CH{\Large<}^{OH}_{NH_2}$$

Acetaldehyde-ammonia
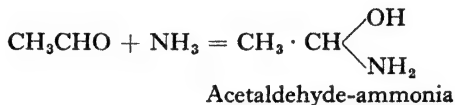
The aldehyde-ammonia crystals are allowed to subside, the clear ethereal liquid is decanted off, and the crystals are filtered off by means of the suction pump and a Buchner funnel. The crystals are then washed with ether and finally dried in a desiccator.

Pure acetaldehyde is obtained from the aldehyde-ammonia as follows:

The aldehyde-ammonia is dissolved in its own weight of water and transferred to a small distilling flask along with a mixture of $1\frac{1}{2}$ parts of concentrated sulphuric acid and 2 parts of water. The distilling flask is placed on the water bath and is connected to a condenser and a receiver cooled in a freezing mixture of ice and salt. The mixture is gradually heated until the water boils, when the flame is removed. The aldehyde-ammonia is decomposed by the acid, and the aldehyde collects in the receiver:

$$2CH_3 \cdot CH{\Large<}^{OH}_{NH_2} + H_2SO_4 = 2CH_3CHO + (NH_4)_2SO_4$$
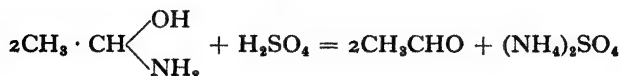
The distillate is then transferred to another distilling flask

containing about 30 gm. of anhydrous calcium chloride and distilled from the water bath heated to 30° C.

Notes: (*a*)—Rubber stoppers must not be used to connect the various parts of the apparatus.

(*b*) The anhydrous aldehyde is stored in a well-stoppered bottle.

(*c*) On account of the inflammable nature of ether, burners must be extinguished before the absorption vessels are filled, and while the crystals are being washed with ether.

(*d*) Ammonia is prepared by gently heating 0·880 ammonia in a flask. The evolved ammonia is dried by passing the vapours up a tower containing either quicklime or soda lime. (See that all the tubes connected to the tower are " free " for the passage of the gas.)

(*e*) Boiling tubes may be used as the absorption vessels.

Properties.—Colourless, mobile, very volatile liquid, sp. gr. 0·801, b. pt. 20·8° C., with peculiar penetrating and suffocating odour, like SO_2. When inhaled it produces cramp in the throat. It is very inflammable, and mixes with water, alcohol, and ether in all proportions.

Reactions.

1. It is slowly oxidized to acetic acid on exposure to air, or with chromic acid:

$$CH_3CHO + O = CH_3COOH$$
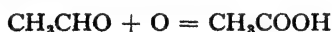
2. It has powerful *reducing properties*. It reduces Tollen's reagent in the form of a silver mirror, and also Fehling's solution (p. 527):

(*a*) $CH_3CHO + Ag_2O = CH_3COOH + 2Ag,$
(*b*) $CH_3CHO + 2CuO = Cu_2O + CH_3COOH.$
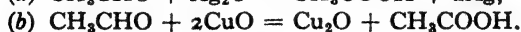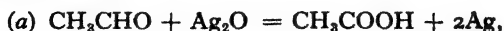
3. It is reduced with sodium amalgam and dilute acid, or zinc dust and acetic acid, to a primary alcohol:

$$CH_3CHO + 2H = CH_3CH_2OH$$
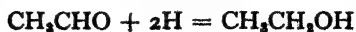
4. It reacts with hydrocyanic acid to form *aldehyde hydro-cyanide* or *ethylidene cyanhydrin*:

$$\begin{array}{c} CH_3 \\ \diagdown \\ H \diagup \end{array} C{=}O + HCN = \begin{array}{c} CH_3 \diagdown \quad \diagup OH \\ C \\ H \diagup \quad \diagdown CN \end{array}$$

Ethylidene
cyanhydrin
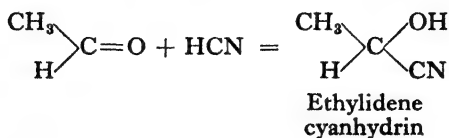
The latter compound on hydrolysis yields lactic acid $CH_3CH \cdot OH \cdot COOH$ (p. 265):

$$\begin{array}{c} CH_3 \\ | \\ CHOH \\ | \\ C\;\overline{|N + H_2 + H|} \\ \quad | \quad\quad | \\ \quad O \quad\;\; OH \end{array} = \begin{array}{c} CH_3 \\ | \\ CHOH \\ | \\ COOH \end{array} + NH_3$$

Ethylidene   Lactic
cyanhydrin   acid
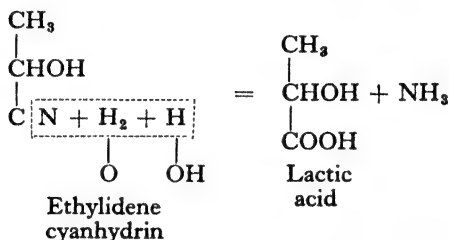
5. If it is shaken with a concentrated solution of alkali bisulphite, colourless crystals of the bisulphite compound separate:

$$\begin{array}{c} CH_3 \\ \diagdown \\ H \diagup \end{array} C{=}O + \begin{array}{c} OH \\ | \\ SO_2Na \end{array} = \begin{array}{c} CH_3 \diagdown \quad \diagup OH \\ C \\ H \diagup \quad \diagdown OSO_2Na \end{array}$$

6. It reacts with hydroxylamine in aqueous solution to form *acetaldoxime*, a crystalline compound:

$$\begin{array}{c} CH_3 \\ \diagdown \\ H \diagup \end{array} C{=}\overline{|O + H_2|}NOH = \begin{array}{c} CH_3 \\ \diagdown \\ H \diagup \end{array} C{=}NOH + H_2O$$

Hydroxylamine   Acetaldoxime
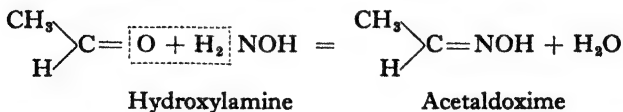
7. With dry ammonia it forms a colourless crystalline substance, aldehyde-ammonia, which is decomposed by acids to re-form the aldehyde (see above, p. 169).

8. With phenylhydrazine it forms a *phenylhydrazone.*

$$CH_3 \!>\! C = O + H \!>\! N \cdot NHC_6H_5 = CH_3 \!>\! C = N \cdot NHC_6H_5 + H_2O$$
$$\quad H \qquad\quad H$$

Phenylhydrazine   Phenylhydrazone
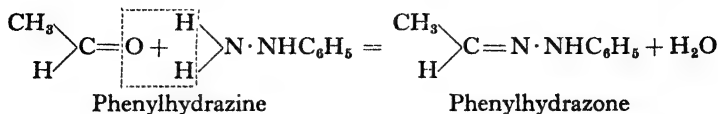
Note.—Phenylhydrazones are usually crystalline substances, sparingly soluble in alcohol. They are easily hydrolysed by acids to the original aldehydes and reduced by sodium amalgam to primary amines:

$$CH_3CH = N \cdot NHC_6H_5 + HOH = CH_3CHO + C_6H_5NH \cdot NH_2,$$
$$CH_3CH = N \cdot NHC_6H_5 + 4H \quad = CH_3CH_2NH_2 + C_6H_5NH_2.$$

Aldehyde phenylhydrazone   Ethylamine   Aniline
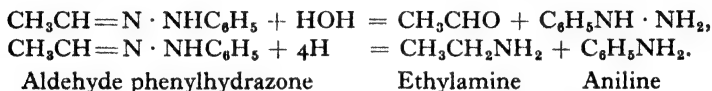
As they have well-defined melting-points, they are employed in the identification of aldehydes.

9. With warm alkalis a vigorous action sets in, and a brown substance, aldehyde resin, is formed.

10. The chlorides of phosphorus yield ethylidene dichloride:

$$CH_3CHO + PCl_5 = CH_3CHCl_2 + POCl_3$$
Ethylidene
dichloride
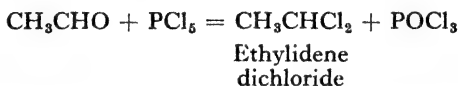
11. Moist chlorine or bromine acts as a substituent:

$$CH_3CHO + 3Cl_2 = 3HCl + CCl_3CHO$$
Chloral
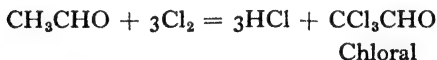
12. It yields a condensation product, *aldol*, when left for some time in contact with dilute HCl, NaOH, K_2CO_3, sodium acetate or zinc chloride.

Condensation is the linking together of molecules through carbon bonds so as to form compounds from which the original substance cannot be regenerated by any simple methods.

Aldol is derived from ALD (aldehyde) and OL (alcohol):

$$CH_3CHO + HCH_2CHO = CH_3CH(OH)CH_2 \cdot CHO$$

Structurally,

Aldol is a colourless inodorous liquid, miscible with water, and shows all the ordinary properties of an aldehyde. It can be distilled under reduced pressure. When distilled under atmospheric pressure, aldol decomposes into water and an unsaturated aldehyde known as *crotonaldehyde*:

Crotonaldehyde is a pungent liquid which can be reduced to *n*-butyl alcohol.

13. It forms *acetal* when heated with alcohol at 100° C.:

$$CH_3CH \begin{array}{|c} O + \end{array} \begin{array}{c|} H \\ H \end{array} \begin{array}{l} OC_2H_5 \\ OC_2H_5 \end{array} = CH_3 \cdot CH(OC_2H_5)_2 + H_2O$$

Acetal

Acetal is a colourless liquid (b. pt. 104°) with an agreeable smell.

14. With H_2S, *thio-aldehyde* is formed:

$$CH_3CHO + H_2S = CH_3CHS + H_2O$$

This aldehyde has an unpleasant aromatic odour and exhibits polymerization.

15. Acetaldehyde exhibits polymerization (see below).

Para-aldehyde, $(CH_3CHO)_3$ or

$$CH_3 \cdot CH\Big\langle{O-CH\Big\langle{\substack{CH_3\\O\\CH_3}}\atop O-CH}\Big\rangle$$
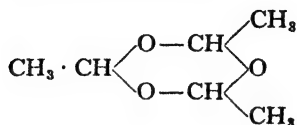
is produced by the addition of small quantities of dilute HCl, concentrated H_2SO_4, H_2SO_3, $ZnCl_2$, or $CoCl_2$ to aldehyde at the ordinary temperature:

$$3C_2H_4O = C_6H_{12}O_3$$

It is a colourless, pleasant-smelling liquid (b. pt. 124° C.), solidifying at 10° C. It is sparingly soluble in water, less soluble in hot water than in cold. It is used in medicine as a soporific. It is not an aldehyde. It does not reduce silver oxide nor does it combine with ammonia or sodium bi-sulphite.

Meta-aldehyde, $(CH_3CHO)_3$,

is produced by the action of acids on aldehyde at a temperature below 0° C. It occurs as white prismatic needles insoluble in water. It sublimes above 100° C. It also shows none of the aldehydic properties.

Both polymers can be reconverted into ordinary aldehyde by distilling with dilute sulphuric acid.

Tests for Acetaldehyde are given in Chap. XXIII, p. 541.

Chloral, Trichloraldehyde, $CCl_3 \cdot CHO$.

Formation.

1. By the action of chlorine on aldehyde in the presence of water and calcium carbonate (p. 172).

2. *Manufacturing process:* By passing a slow stream of dry chlorine into alcohol, first at the ordinary temperature and then at about 60–65° C. until hydrogen chloride is no

longer evolved. The chlorination of the alcohol takes about two weeks, the chlorine acting both as a chlorinating and an oxidizing agent:

$$CH_3CH_2OH + Cl_2 = CH_3CHO + 2HCl,$$
$$CH_3CHO + 3Cl_2 = CCl_3CHO + 3HCl.$$
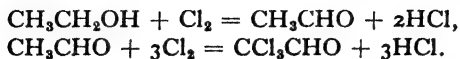
The chloral formed reacts immediately with the alcohol present to form a crystalline additive compound known as chloral alcoholate:

$$CCl_3 \cdot CHO + C_2H_5OH = CCl_3 \cdot CH{\Large\langle}^{OH}_{O \cdot C_2H_5}$$

Chloral alcoholate
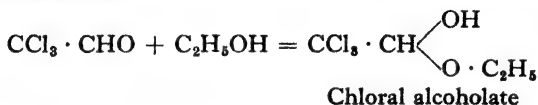
This substance is separated and distilled with concentrated sulphuric acid; chloral distils over as a heavy oil:

$$CCl_3CH(OH)OC_2H_5 + H_2SO_4 = CCl_3CHO + C_2H_5HSO_4 + H_2O.$$
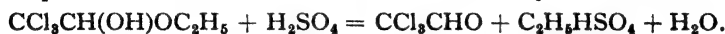
Structurally,
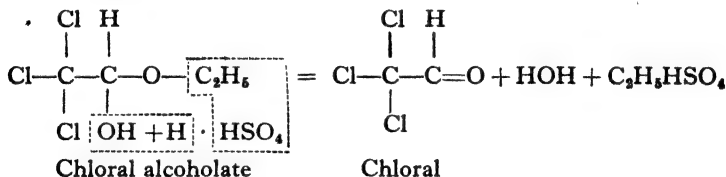
The distillate is purified by recrystallization from water; chloral hydrate separates:
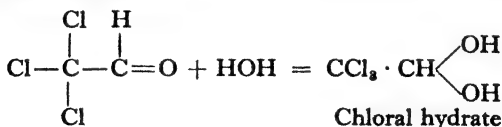
This compound is separated, dried and distilled with concentrated sulphuric acid, the portion distilling over between 97° and 99° C. being pure chloral.

Properties.—Oily liquid with sharp characteristic odour, b. pt. 98° C., sp. gr. 1·54. It reduces Tollen's reagent and

combines with $NaHSO_3$, NH_3, HCN, and acetic acid like an aldehyde. It combines readily with water to form a crystalline compound known as *chloral hydrate*, $CCl_3CHO . H_2O$ or $CCl_3CH(OH)_2$.

Chloral hydrate forms monoclinic colourless crystals, m. pt. 57° C., b. pt. 97·50° C. It does not contain the aldehyde group, for it does not polymerize nor give Schiff's Test (p. 167). When heated with alkali, both chloral and chloral hydrate are decomposed, giving chloroform and a formate:

$$CCl_3CHO + KOH = CHCl_3 + HCOOK$$

Uses.—Taken internally in doses of from 0·6 to 2 gm. it acts as a soporific. In larger doses it acts as an anæsthetic. It is a habit-forming drug.

Constitution of Acetaldehyde.

The constitution of the aldehydes is based on a study of their characteristic reactions.

1. One oxygen atom can be replaced by two chlorine atoms, e.g. $CH_3CHO \rightarrow CH_3CHCl_2$. Hence the oxygen is not united to a carbon atom in the same way as a hydroxyl group is, and must be linked by its two valencies. This indicates the presence of a $=C=O$ group, e.g. $H_2C=O$ and $CH_3—HC=O$.

No hydrogen is removed, and therefore no hydroxyl group is present (contrast the alcohols).

2. Aldehydes are formed by the oxidation of primary alcohols, two hydrogen atoms being removed. The $=CO$ group must therefore be present at the end of the carbon chain, e.g.

$$\overset{\displaystyle H}{\underset{\displaystyle H}{CH_3—C—O}}\,\fbox{H + O} = CH_3—\overset{\displaystyle H}{C}=O + HOH$$
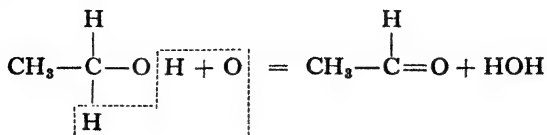
3. The formation of additive and oxidation products points to the constitution of formaldehyde and acetaldehyde being respectively

$$\underset{H}{\overset{H}{H-C=O}}, \quad H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{C}=O$$
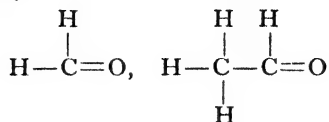
Coupling.—On considering the characteristic properties of acetaldehyde and other compounds it will be observed that there are a number of cases in which the reaction is accompanied by the elimination of a molecule of some simple inorganic substance such as water or iodine. Such a reaction is known as *coupling* (Gerhardt, 1839).

Examples.—1. Conversion of methyl iodide into ethane (p. 59).

2. Conversion of aldehyde into crotonaldehyde (p. 173).

3. Formation of acetal, acetaldoxime, phenylhydrazone, &c. (pp. 172, 173).

4. Formation of acetoxime, thio-acetone, &c. (pp. 182, 183).

QUESTIONS

1. How may acetaldehyde be prepared? Describe its principal chemical properties and show how it may be converted into ethyl alcohol, lactic acid, and acetaldoxime.

(*Chemists and Druggists Qual.*)

2. Describe the preparation of each of the following: ethyl acetate, an aqueous solution of acetic aldehyde, ethylene bromide.

3. What are the characteristic aldehyde reactions?
How would you prepare a specimen of aldehyde-ammonia, employing ethyl alcohol as the starting point?

4. How would you prepare an aqueous solution of formaldehyde? Compare and contrast the behaviour of formaldehyde and acetaldehyde with (*a*) ammonia, (*b*) potassium hydroxide, (*c*) ammoniacal silver nitrate, (*d*) gelatine.

5. Describe and explain the experiments in which you have seen an alcohol oxidized to (a) an aldehyde, (b) an acid, (c) carbon dioxide and water.

What are the properties of (i) acetaldehyde, (ii) formalin, (iii) paraform, (iv) chloral hydrate?

6. It is stated that " the products of a reaction are largely determined by the conditions under which the reaction takes place ". Discuss this statement in connexion with the reactions between:

(a) chloral hydrate and potassium hydroxide;

(b) ethyl alcohol and sulphuric acid;

(c) ethyl iodide and sodium hydroxide.

7. Explain the meaning of the following and give two examples in each case: (a) isomerism, (b) hydrolysis, (c) polymerization.

8. What is chloral hydrate? How is it prepared? What chemical changes take place when it reacts with: (a) sodium hydroxide, (b) sulphuric acid, (c) nitric acid?

9. Discuss the general properties of aldehydes and acids, and state how a member of one class may be converted into a member of the other.

10. What products are formed by the interaction of:

(a) acetylene and ammoniacal cuprous chlorine;

(b) formic acid and concentrated sulphuric acid,

(c) sodium ethoxide and ethyl iodide,

(d) acetaldehyde and phosphorus pentachloride?

Ketones

The names of the simple ketones are derived from the acids which yield them, e.g. acetone from acetic acid.

They have the general formula

$$C_nH_{2n+2}CO.$$
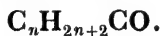
They are, however, more usually named by adding the suffix *ketone* to the name of the alkyl groups present, e.g. $CH_3 . CO . C_2H_5$, methyl ethyl ketone. As in the case of the ethers, there are both simple and mixed ketones.

Acetone, Dimethyl ketone, CH_3COCH_3.

Occurrence.—In pyroligneous liquor (p. 103) or crude wood spirit from the distillation of cellulose and other carbohydrates. It is found in small quantities in the human body, especially in urine and blood. In pathological cases of diabetes the percentage of acetone in the urine is considerably increased.

Formation.

Laboratory Method.—By the dry distillation of calcium acetate:

$$\begin{matrix} CH_3COO \\ CH_3COO \end{matrix} \Big\rangle Ca = CH_3COCH_3 + CaCO_3$$
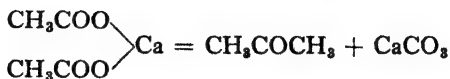
The acetone obtained is impure and is purified by the addition of sodium bisulphite solution. The acetone sodium

bisulphite deposited is filtered off, and decomposed with sodium carbonate. The acetone is recovered by distillation and is finally dehydrated over solid calcium chloride and again distilled.

$$
\begin{array}{l}
CH_3 \\
\quad\diagdown \\
\quad\quad C \\
\quad\diagup \quad \diagdown \\
CH_3 \quad\quad O\;H
\end{array}
\begin{array}{|c c|}
\hline
SO_3Na & Na \\
 & | \\
 & | \\
\hline
\end{array}
\begin{array}{l}
O \\
| \\
O\;C \\
| \\
O
\end{array}
= 2
\begin{array}{l}
CH_3 \\
\quad\diagdown \\
\quad\quad C=O + 2Na_2SO_3 + CO_2 \\
\quad\diagup \qquad\qquad\qquad\qquad + H_2O \\
CH_3
\end{array}
$$
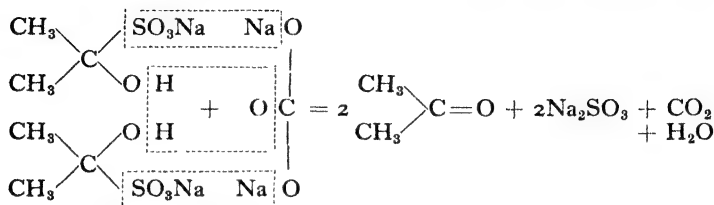
Acetone sodium bisulphite

2. By the decomposition of dichlorides containing the group —C—CCl₂—C— with water:

$$(CH_3)_2CCl_2 + H_2O = (CH_3)_2CO + 2HCl$$
Acetone chloride
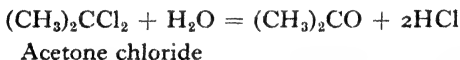
3. By the oxidation of the *secondary alcohol*, isopropyl alcohol, with potassium dichromate and sulphuric acid:

$$CH_3\ CH(OH)\ CH_3 + O = CH_3 \cdot CO \cdot CH_3 + H_2O$$

4. *Manufacturing Processes.*

A. *Fermentation Process.*—By the action of a particular species of bacterium (*bacillus macerans*) on starch (obtained mainly from maize, although starch from other grains and from potatoes can be used). The starch is fermented by the bacillus into acetone, ethyl alcohol and *n*-butyl alcohol.

B. *Catalytic Processes.*—(i) *Roka Process:* By passing ethyl alcohol vapour saturated with steam over catalysts heated to 500° C. The catalysts used are the oxides of heavy metals, e.g. PbO. The reaction may be represented as follows:

$$2C_2H_5OH + H_2O = (CH_3)_2CO + CO_2 + 4H_2$$

The hydrogen formed is utilized to convert crotonaldehyde into butyl alcohol:

$$CH_3CH{=}CH \cdot CHO + 4H = CH_3CH_2CH_2CH_2OH$$
Crotonaldehyde $\qquad$ n-butyl alcohol
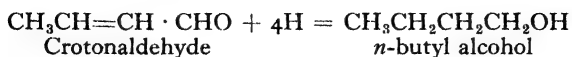
(ii) By passing acetic acid vapour over catalysts heated almost to a red heat. The catalysts used are the oxides of the alkaline earth metals, e.g. CaO:

$$\begin{matrix} CH_3COOH \\ + \\ CH_3COOH \end{matrix} = \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}{>}C{=}O + CO_2 + H_2O$$
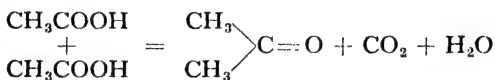
Commercial acetone is purified by fractionating over lime, or by conversion into the bisulphite compound, as already described.

The extraction of acetone from crude wood spirit has now been superseded by one or other of the above processes.

Properties.—Colourless mobile liquid, with a pleasant ethereal odour, b. pt. 57° C., sp. gr. 0·798. It is miscible with water, alcohol, and ether in all proportions. Several of its chemical properties resemble those of aldehyde.

Uses.—In the manufacture of chloroform, iodoform and sulphonal; as a solvent for acetylene; in gelatinizing nitro-cellulose for celluloid and smokeless powders. It is a good solvent and is used for purifying and recrystallizing many organic compounds.

Reactions:

1. It is oxidized only by moderately powerful agents (e.g. $K_2Cr_2O_7$) into an acid containing a smaller number of carbon atoms in the molecule:

$$CH_3COCH_3 + 2O_2 = CH_3COOH + CO_2 + H_2O$$

2. On reduction it is converted into secondary propyl alcohol:

$$CH_3COCH_3 + 2H = (CH_3)_2CH \cdot OH$$
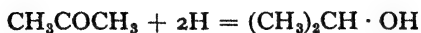
3. It reacts with hydrocyanic acid to form acetone cyanhydrin:

$$CH_3COCH_3 + HCN = CH_3 \cdot C(OH) \cdot CN \cdot CH_3$$
Acetone cyanhydrin
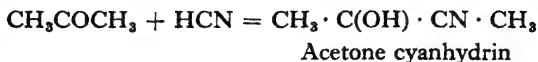
4. When shaken with a concentrated solution of sodium bisulphite it forms a colourless crystalline compound:

$$\begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \diagup \end{array} CO + NaHSO_3 = \begin{array}{c} CH_3 \diagdown \quad \diagup OH \\ \quad C \\ CH_3 \diagup \quad \diagdown SO_2 \cdot ONa \end{array}$$
Acetone sodium bisulphite
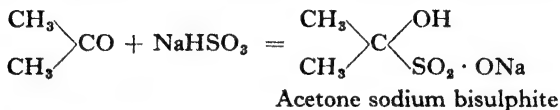
Acetone sodium bisulphite is readily soluble in water and is easily decomposed by dilute acids and alkalis, acetone being regenerated.

5. It reacts with hydroxylamine in aqueous solution, forming *acetoxime*:

$$(CH_3)_2CO + NH_2OH = (CH_3)_2C{=}NOH + H_2O$$
Acetoxime
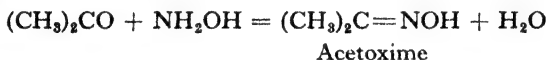
Acetoxime is a crystalline substance melting at 59° C.

6. It reacts with PCl_5 to form acetone chloride (β-dichloropropane):

$$(CH_3)_2CO + PCl_5 = POCl_3 + (CH_3)_2CCl_2(\overset{\alpha}{CH_3} \cdot \overset{\beta}{CCl_2} \cdot \overset{\alpha}{CH_3})$$
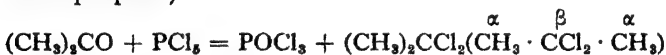
7. It reacts with phenylhydrazine to form acetone phenylhydrazone:

$$(CH_3)_2C\,\boxed{O + H_2}\,N \cdot NH \cdot C_6H_5 = (CH_3)_2\,CN \cdot NHC_6H_5 + H_2O$$
Phenylhydrazine   Acetone phenylhydrazone
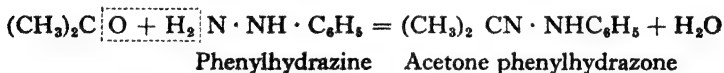
Note.—Many of the ketonic phenylhydrazones are liquids of definite boiling-point.

8. It yields complex condensation products with ammonia:

$$2(CH_3)_2CO + NH_3 = C_6H_{11}ONH_2 + H_2O$$
Diacetone amine
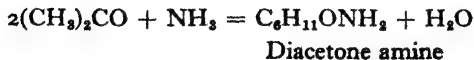
9. With H_2S it forms thio-acetone:

$$(CH_3)_2CO + H_2S = (CH_3)_2CS + H_2O$$
$$\text{Thio-acetone}$$
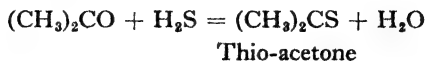
10. It forms a condensation product, *mesitylene* or *tri-methyl benzene*. Mesitylene is formed when acetone is mixed with twice its weight of moderately strong sulphuric acid and distilled; a liquid boiling at 165° C. passes over. Water is eliminated from the carbonyl group of one molecule and a methyl group of another:

Mesityl oxide
(intermediate product)
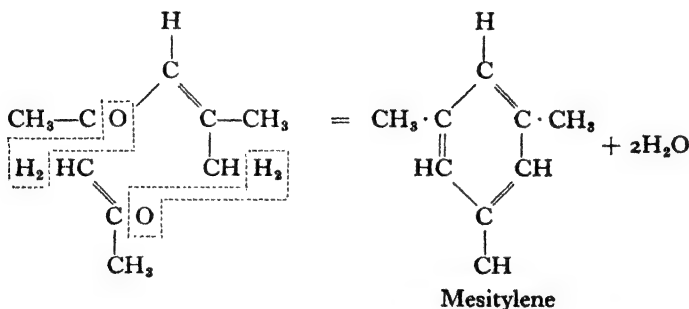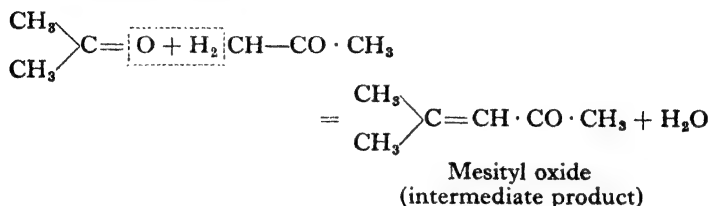
Mesitylene

Mesityl oxide, the intermediate product, is an *unsaturated ketone* possessing properties of a ketone and also of an olefine. It forms additive compounds at the junction of the double bond.

Mesitylene, the final product, is an aromatic hydrocarbon formed by the elimination of three molecules of water from three molecules of acetone.

Acetone, however, differs from aldehyde in the following respects:

(*a*) It does not give Fehling's test.
(*b*) It does not give Schiff's test immediately.
(*c*) It does not undergo polymerization.
(*d*) It does not reduce Tollen's reagent.
(*e*) It does not give a resin with KOH.
(*f*) It gives the Iodoform test.

Tests for Acetone are given in Chap. XXII, p. 529.

Constitution of Acetone.

Its method of formation from isopropyl alcohol by oxidation indicates that an oxygen atom is directly attached by a double bond to a carbon atom:

$$\begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \diagup \end{array}\!\!CHOH + O = \begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \diagup \end{array}\!\!C{=}O + H_2O$$
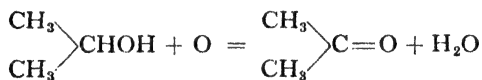
This constitution is in agreement with the chemical behaviour, for:

1. It contains no —OH group, since it does not form salts with acids.

2. The oxygen can be displaced by two chlorine atoms, using PCl_5.

3. All its characteristic reactions indicate the presence of the carbonyl or ketone group $\diagdown C{=}O$.

Mixed Ketones

Methyl ethyl ketone is the simplest example of a mixed ketone. It occurs as a by-product in the preparation of acetone from wood spirit.

Formation.—1. By the distillation of a mixture of calcium acetate and calcium propionate:

$$CH_3CO \cdot O \qquad O \cdot OC \cdot C_2H_5$$
$$| \qquad |$$
$$Ca \qquad Ca \qquad = \quad 2CH_3 \cdot CO \cdot C_2H_5 + 2CaCO_3$$
$$| \qquad | \qquad\qquad \text{Methyl ethyl}$$
$$CH_3 CO \cdot O \qquad O \cdot OC \cdot C_2H_5 \qquad \text{ketone}$$

Calcium acetate   Calcium propionate
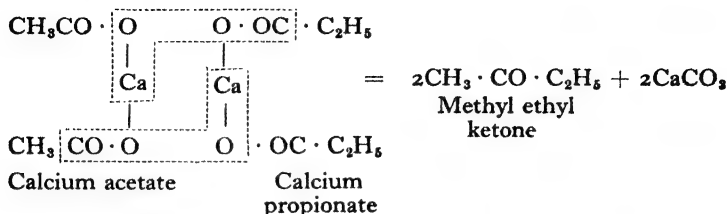
2. From normal butylene by the addition of water, followed by reduction.

$$CH_3 \cdot CH_2 \cdot CH = CH_2 \xrightarrow{(+HOH)} CH_3 \cdot CH_2 \cdot CHOH \cdot CH_3$$
Butylene

$$\xrightarrow{(-2H)} CH_3 \cdot CH_2 \cdot CO \cdot CH_3$$
Methyl ethyl ketone
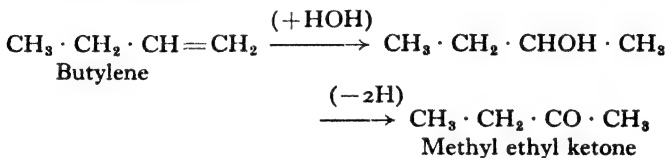
Properties.—Colourless liquid, b. pt. 81° C., similar to acetone.

Reactions.—1. On reduction it forms secondary butyl alcohol:

$$CH_3 \cdot CH_2 \cdot C \cdot CH_3 \qquad\qquad CH_3 \cdot CH_2 \cdot CH \cdot CH_3$$
$$\| \qquad +H_2 \quad = \qquad\qquad |$$
$$O \qquad\qquad\qquad\qquad\qquad OH$$
Secondary butyl alcohol
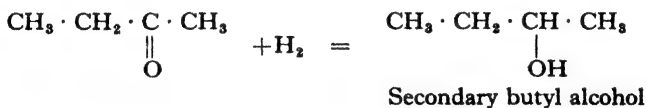
2. On oxidation it is converted into a mixture of acetic, propionic, and carbonic acids.

3. On oxidation with selenium oxide, a yellow liquid, *diacetyl*, $CH_3 . CO . CO . CH_3$, is obtained.

$$CH_3 \cdot CH_2 \cdot CO \cdot CH_3 + O_2 = CH_3 \cdot CO \cdot CO \cdot CH_3 + H_2O$$
Diacetyl
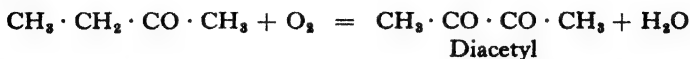
4. It is converted into *acetoin*, $CH_3 . CHOH . CO . CH_3$, by a special reaction. Acetoin is found in butter, to which it imparts its flavour.

5. It reacts with nitrous acid to form *diacetyl monoxime*. This monoxime on hydrolysis with hydrochloric acid is converted into *diacetyl*, which on treatment with hydroxylamine hydrochloride yields the original ketone.

$$(\text{HCl} + \text{H}_2\text{O})$$

$$CH_3 \cdot C\fbox{$H_2 + O$}N \cdot OH \qquad CH_3 \cdot C = N \cdot OH \qquad CH_3 \cdot C = O$$
$$\mid \qquad\qquad\qquad\qquad\qquad \mid \qquad\qquad\qquad\qquad \mid$$
$$CH_3 \cdot C = O \qquad\qquad\rightarrow\quad CH_3 \cdot C = O \quad\rightarrow\quad CH_3 \cdot C = O$$

Methyl ethyl ketone   Diacetyl monoxime   Diacetyl

$$CH_3 - C = \fbox{$O + OH \cdot N$}H_2 \cdot HCl \qquad CH_3 - CH_2 \; + HNO_2$$
$$\mid \qquad\qquad\qquad\qquad\qquad = \qquad\qquad \mid$$
$$CH_3 - C = O \qquad\qquad\qquad\qquad CH_3 - C = O + HCl$$
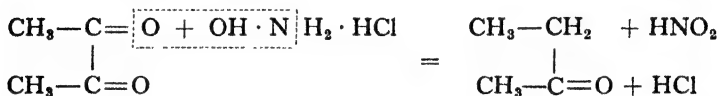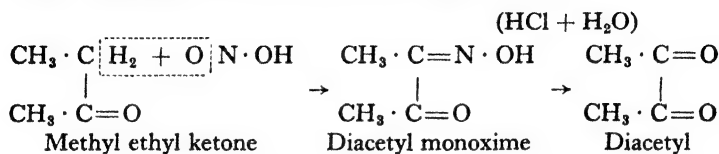
Methyl ethyl ketone was formerly used as a solvent in the preparation of cordite from gun cotton and nitroglycerine. Acetone is now used for this purpose.

Dimethylglyoxime, Diacetyldioxime,

$$CH_3 - C = NOH$$
$$\mid$$
$$CH_3 - C = NOH$$
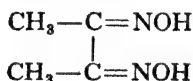
is a white crystalline substance, m. pt. 236° C. It is soluble in alcohol and is used as a test for nickel in qualitative analysis, precipitating the metal as a red crystalline compound of composition $C_8H_{14}N_4O_4Ni$.

SUMMARY

Aldehydes

$$\underset{H}{\overset{R}{>}}C=O, \text{ e.g. } \underset{H}{\overset{CH_3}{>}}C=O$$

1. *Hydrogen.*

$$\underset{H}{\overset{R}{>}}C=O + H_2 = R \cdot CH_2OH$$
$$\text{(Primary alcohol)}$$

2. *Oxygen.*

$$\underset{H}{\overset{R}{>}}C=O + O = R \cdot COOH$$

3.
$$\underset{H \cdot COO \cdot \frac{1}{2}Ca}{CH_3CO \cdot O \cdot \frac{1}{2}Ca} = CH_3CHO + CaCO_3$$

4. *Hydrocyanic Acid.*

$$\underset{H}{\overset{R}{>}}C=O + HCN = \underset{H}{\overset{R}{>}}C\underset{CN}{\overset{OH}{<}}$$

5. *Sodium Bisulphite.*

$$\underset{H}{\overset{R}{>}}C=O + NaHSO_3 = \underset{H}{\overset{R}{>}}C\underset{OSO_2 \cdot Na}{\overset{OH}{<}}$$

Ketones

$$\underset{R}{\overset{R}{>}}C=O, \text{ e.g. } \underset{CH_3}{\overset{CH_3}{>}}C=O$$

1.
$$\underset{R}{\overset{R}{>}}C=O + H_2 = \underset{R}{\overset{R}{>}}CH \cdot OH$$
$$\text{(Secondary alcohol)}$$

2.
$$\underset{CH_3}{\overset{R}{>}}C=O + 4O = R \cdot COOH + CO_2 + H_2O$$

3.
$$\underset{CH_3 \cdot COO \cdot \frac{1}{2}Ca}{CH_3CO \cdot O \cdot \frac{1}{2}Ca} = (CH_3)_2CO + CaCO_3$$

4.
$$\underset{R}{\overset{R}{>}}C=O + HCN = \underset{R}{\overset{R}{>}}C\underset{CN}{\overset{OH}{<}}$$

5.
$$\underset{R}{\overset{R}{>}}C=O + NaHSO_3 = \underset{R}{\overset{R}{>}}C\underset{OSO_2 \cdot Na}{\overset{OH}{<}}$$

Left column:

6. *Hydroxylamine.*

$$\overset{R}{\underset{H}{>}}C=O + \boxed{H_2}\,NOH \rightarrow \overset{R}{\underset{H}{>}}C=N\cdot OH$$

7. *Phenylhydrazine.*

$$\overset{R}{\underset{H}{>}}C=O + \boxed{H_2}\,N\cdot NH\cdot C_6H_5$$

$$\rightarrow \overset{R}{\underset{H}{>}}C=N\cdot NH\cdot C_6H_5$$

$R=CH_3$ Aldehyde phenylhydrazone

8. *Grignard's Reagent.*

$$\overset{R}{\underset{H}{>}}C=O + MgI\cdot CH_3 = \overset{R}{\underset{H}{>}}C\overset{OMgI}{\underset{CH_3}{<}}$$

$$\overset{R}{\underset{H}{>}}C\overset{OH}{\underset{CH_3}{<}}$$

(Secondary alcohol)

$$+\ Mg\overset{OH}{\underset{I}{<}}$$

9. *Phosphorus Pentachloride.*

$$\overset{R}{\underset{H}{>}}C=O + PCl_5 = \overset{R}{\underset{H}{>}}C=Cl_2 + POCl_3$$

Right column:

6. $$\overset{R}{\underset{R}{>}}C=O + \boxed{H_2}\,NOH \rightarrow \overset{R}{\underset{R}{>}}C=N\cdot OH$$

7. $$\overset{R}{\underset{R}{>}}C=O + \boxed{H_2}\,N\cdot NH\cdot C_6H_5$$

$$\rightarrow \overset{R}{\underset{R}{>}}C=N\cdot NH\cdot C_6H_5$$

$R=CH_3$ Acetone phenylhydrazone

8. $$\overset{R}{\underset{R}{>}}C=O + MgI\cdot CH_3 = \overset{R}{\underset{R}{>}}C\overset{OMgI}{\underset{CH_3}{<}}$$

$$\overset{R}{\underset{R}{>}}C\overset{OH}{\underset{CH_3}{<}}$$

(Tertiary alcohol)

$$+\ Mg\overset{OH}{\underset{I}{<}}$$

9. $$\overset{R}{\underset{R}{>}}C=O + PCl_5 = \overset{R}{\underset{R}{>}}C=Cl_2 + POCl_3$$

DIFFERENCES BETWEEN ALDEHYDES AND KETONES

A. Aldehyde ammonia:

$$CH_3CHO + NH_3 = CH_3 \cdot CH \underset{NH_2}{\overset{OH}{<}}$$
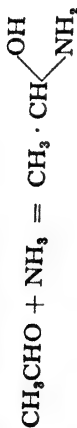
B. Give a resin with KOH.

C. Reduce Fehling's solution and Tollen's reagent.

D. Do not give the iodoform test.

E. Form polymers.

F. Give Schiff's rosaniline test.

G. Form aldol condensation products: e.g.

$$CH_3 - \underset{\underset{O}{\overset{||}{}}}{\overset{\overset{H}{|}}{C}} + CH_2 - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} = CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}} - CH_2CHO$$

H. Form acetals:

$$CH_3CHO + 2C_2H_5OH = CH_3 \cdot CH (OC_2H_5)_2 + H_2O$$

A. More complex products:

$$2 \,\, CH_3 \underset{CH_3}{\overset{CH_3}{>}} CO + NH_3 = C_6H_{11}ONH_2 + H_2O$$
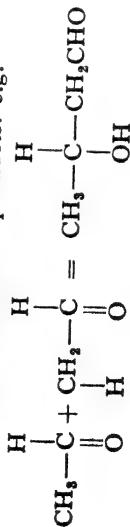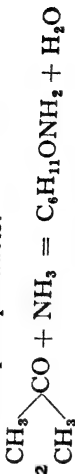
B. Do not give a resin with KOH.

C. Do not reduce these solutions.

D. Give the iodoform test.

E. Do not form polymers.

F. Do not give Schiff's test, except in some cases on standing.

G. Capable of yielding condensation products, but of a different type.

QUESTIONS

1. What reactions would you use in order to test for the presence of an organic compound of each of the following groups: (*a*) Hydroxyl — OH, (*b*) Aldehyde — CHO, (*c*) Ketone $>$CO, (*d*) Amino — NH_2? (*Pre. Med.*)

2. Indicate by reference to examples the meaning of each of the following: hydrolysis, polymerization, a bisulphite compound, an aldehyde ammonia.

3. Compare and contrast the behaviour of aldehydes and ketones with: (*a*) hydroxylamine, (*b*) oxidizing agents, (*c*) nascent hydrogen, (*d*) alcohol. Illustrate by reference to examples.

4. Give equations illustrating the general methods of formation and the general chemical properties of aldehydes. In what respects do the reactions of ketones differ from those of aldehydes? (*Chemists and Druggists Qual.*)

5. Give examples of (*a*) an aldehyde, (*b*) a ketone, (*c*) an aldehyde ammonia, (*d*) a bisulphite derivative of an aldehyde or of a ketone.

By what tests could you distinguish an aldehyde from a ketone?

6. Describe two methods by which acetone may be prepared.

How does acetone react with (*a*) sodium bisulphite, (*b*) sodium amalgam and water?

7. Mention three types of organic compound in which the keto (or carbonyl) group CO is present. Give a simple example of each type, and indicate in each case methods by which the presence of the CO group could be shown. (*Inter. B. Pharm.*)

8. Show, by dealing with the derivatives of methane and ethane, the connexions which exist between the following classes of oxygen derivatives: alcohols, ethers, aldehydes, ketones, acids, ethereal salts.

9. Compare and contrast the behaviour of the aldehydes and ketones with each of the following reagents: Fehling's solution, nascent hydrogen, an oxidizing agent, phenylhydrazine.

10. How may the following be obtained from acetic acid: acetone, acetaldehyde, acetamide, methane?

11. How would you distinguish between the following pairs of substances:

(*a*) a ketone and an aldehyde,

(*b*) a primary and a secondary alcohol,

(*c*) a primary and a secondary amine?

(*Oxford Higher School Cert.*)

The Fatty Acids

The fatty acids form a homologous series with the general formula

$$C_nH_{2n+1}COOH \quad \text{or} \quad C_nH_{2n}O_2.$$

They may be regarded as derivatives of the paraffins, the alcohols, or the aldehydes. Many of the members of this group occur in large quantities as *glycerol esters* in animal fats and animal and vegetable oils; hence the name fatty acid.

The following table contains the names of some of the acids which will be mentioned.

Name		Derivation	B. pt.
Formic acid	HCOOH	*Formica*, an ant	101° C.
Acetic acid	CH_3COOH	*Acetum*, vinegar	118
Propionic acid	C_2H_5COOH	πρῶτος (*protos*) first; πιων (*pion*), fat	141
Butyric acid	C_3H_7COOH ✓	*Butyrum*, butter	162
Palmitic acid	$C_{15}H_{31}COOH$	*Palma*, a palm tree	269
Stearic acid	$C_{17}H_{35}COOH$	στέαρ (*stear*), suet	287

The group characteristic of organic acids is the **carboxyl** group $-COOH$.

These acids are all monobasic, and it is the hydrogen of the carboxyl group that is replaced when salts are formed.

Formic Acid (*Acidum formicum*), HCOOH.

Occurrence.—In stinging nettles, in ants, especially *Formica rufa*, in the processionary caterpillar (*Bombyx processionea*), in the fruit of the soap tree (*Sapindus saponaria*);

also in small quantities in perspiration, urine, and extract of meat.

Formation.

1. By distilling red ants with water.

2. By heating oxalic acid with glycerol, or by heating oxalic acid alone.

Place 30 gm. of crystallized oxalic acid and 50 c.c. of glycerol in a retort connected with a condenser. Heat to 100 to 110° C.; carbon dioxide is evolved and formic acid distils over. Continue heating until action ceases. Further addition of oxalic acid produces a further quantity of more concentrated formic acid. This process is theoretically continuous.

The reaction takes place in stages. The first product is glyceryl monoxalate or monoxalin:

$$
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
+
\begin{array}{c}
COOH \\
| \\
COOH
\end{array}
=
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2O \cdot CO \cdot COOH \\
\text{Glyceryl} \\
\text{monoxalate}
\end{array}
+ H_2O \rightarrow
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OCHO \\
\text{Monoformin}
\end{array}
+ CO_2
$$
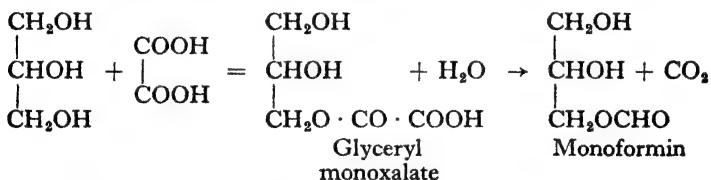
The monoxalin decomposes into glyceryl monoformate (monoformin) and carbon dioxide. The addition of more oxalic acid liberates formic acid; this distils over and glyceryl monoxalate is re-formed:

$$
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2O - C
\begin{array}{c}
O \\
H
\end{array}
\end{array}
+
\begin{array}{c}
COOH \\
| \\
COOH
\end{array}
=
\begin{array}{c}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2O \cdot CO \cdot COOH
\end{array}
+ H \cdot COOH
$$
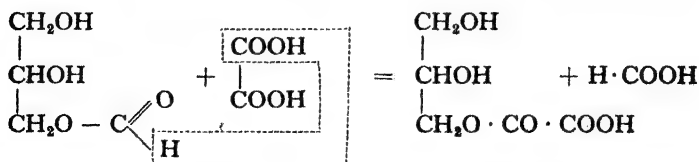
The monoxalate again decomposes and the reactions continue as shown.

Anhydrous formic acid is formed by boiling the distillate with excess of litharge or lead carbonate and filtering while hot. On cooling, crystals of lead formate separate. These are dried, placed in an upright Liebig condenser between plugs of cotton wool and heated by passing steam through the outer tube; dry H_2S is then passed over the lead formate, and formic acid collects in the receiver:

$$2HCOOH + PbO = (HCOO)_2Pb + H_2O,$$
$$(HCOO)_2Pb + H_2S = 2HCOOH + PbS.$$
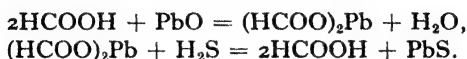
The product is finally redistilled.

3. (a) *Commercial Method.*—Carbon monoxide (from producer gas) under 6–8 atmospheres pressure is passed into a 10 per cent solution of caustic soda heated to 160° C., or over a mixture of calcined soda ash and dry slaked lime heated to 170° C.:

$$CO + NaOH = HCOONa,$$
$$2CO + Na_2CO_3 + Ca(OH)_2 = 2HCOONa + CaCO_3.$$
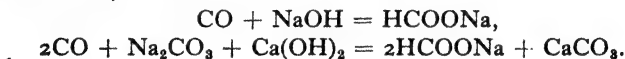
(b) By the action of moist carbon dioxide upon metallic potassium:

$$2K + 2HOH = 2KOH + 2H,$$
$$2CO_2 + 2H + 2KOH = HCOOK + KHCO_3 + H_2O.$$

The acid may be obtained from the potassium formate by distillation with dilute sulphuric acid.

4. By the oxidation of methyl alcohol or formaldehyde by air with platinum black, or by means of potassium dichromate or manganese dioxide and dilute sulphuric acid:

$$CH_3OH + 2O = HCOOH + H_2O,$$
$$HCHO + O = HCOOH.$$
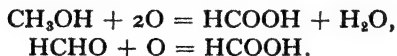
5. By heating hydrocyanic acid with a dilute mineral acid or with a solution of an alkali; ammonia and formic acid are produced:

$$HCN + 2H_2O = HCOOH + NH_3$$

In the presence of a mineral acid the ammonium salt of the

acid is produced, and if an alkali is present the formate of the alkali metal results.

6. By decomposing chloroform with alcoholic potash or chloral with caustic alkalis:

$$CHCl_3 + 4KOH = 3KCl + HCOOK + 2H_2O,$$
$$CCl_3CHO + NaOH = CHCl_3 + HCOONa.$$
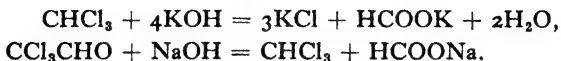
7. By treating a concentrated solution of ammonium carbonate with sodium amalgam:

$$(NH_4)_2CO_3 + 2H = HCOONH_4 + H_2O + NH_3$$

According to this method, and also by the action of moist carbon dioxide on potassium, formic acid appears to be a reduction product of carbonic acid:

$$H_2CO_3 = HCOOH + O$$

Properties.—Colourless mobile hygroscopic liquid, m. pt. 8·3° C., b. pt. 101°, sp. gr. 1·241. It has an irritating odour. When dropped on the skin it causes extreme pain and produces blisters. It is miscible with water and alcohol in all proportions. It gives an acid reaction with litmus and behaves like a weak mineral acid. It decomposes carbonates and dissolves certain metallic oxides. It has *reducing pro-perties*; it precipitates silver from warm solutions of ammoniacal silver hydroxide (Tollen's reagent):

$$HCOOH + Ag_2O = 2Ag + CO_2 + H_2O$$
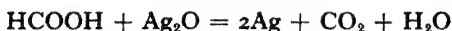
and reduces mercuric chloride to mercurous chloride.

It is decomposed by concentrated sulphuric acid, producing carbon monoxide:

$$HCOOH - HOH = CO$$

When heated alone at 160° C. in closed vessels it yields carbon dioxide and hydrogen:

$$HCOOH = CO_2 + H_2$$
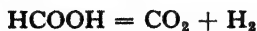
It yields salts called *formates*, which are produced by neutralizing the acid with alkalis, hydroxides, &c., or by double decomposition. The formates are all soluble in water, except those of lead and silver, which are only moderately soluble. These salts are decomposed by concentrated sulphuric acid, evolving carbon monoxide, and by dilute mineral acids, yielding formic acid. The alkali salts are deliquescent and when heated to 250° C. they form oxalates:

$$\begin{matrix} HCOONa \\ HCOONa \end{matrix} = \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2$$

Sodium oxalate
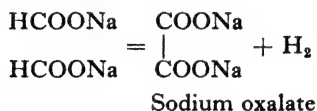
Ammonium formate yields *formamide* (p. 208) when heated to 230° C.:

$$HCOONH_4 = HCO \cdot NH_2 + H_2O$$

Formamide

Silver formate is formed by precipitation on adding silver nitrate to a neutral concentrated solution of a formate. It rapidly decomposes, depositing silver:

$$2HCOOAg = 2Ag + 2CO_2 + H_2$$

Uses.—Formic acid is a powerful antiseptic and hence is used to preserve fruit juices. As it is now cheaply made, it is displacing acetic acid, lactic acid and argol in the manufacture of leather, in dyeing woollen textiles, &c. It is added to the mash in brewing to stimulate the fermentative power of the yeast, preserving the diastase in the malt and preventing certain acid-producing bacteria from developing.

Tests for Formic Acid and Formates are given in Chap. XXIII, p. 544.

Constitution of Formic Acid.

Formic acid is produced from methyl alcohol by the substitution of one oxygen atom for two atoms of hydrogen, and must therefore have the following constitution:

$$\text{H}-\overset{\displaystyle \text{H}}{\underset{\displaystyle \text{H}}{\text{C}}}-\text{OH} \rightarrow \text{(I)} \; \overset{\displaystyle \text{O}}{\underset{\displaystyle \text{H}}{\text{C}}}-\text{OH} \quad \text{or} \quad \text{(II)} \; \text{H}-\overset{\displaystyle \text{H}}{\text{C}}\diagdown_{\text{O}}^{\text{O}}$$
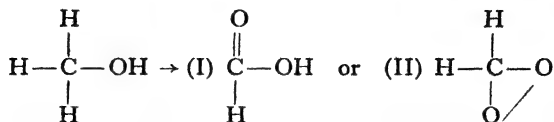
The formula (II) does not correctly indicate the behaviour of formic acid. It represents the two hydrogen atoms of formic acid as being in the same state of combination. Only one hydrogen atom, however, is readily displaced by metals, and this hydrogen atom must be attached to an oxygen atom in a hydroxyl group, as in the monohydric alcohols from which it is formed.

Moreover, formic acid behaves in some respects like an aldehyde, and thus should contain the group $-\overset{\displaystyle \text{H}}{\text{C}}=\text{O}.$ This is shown by its methods of formation:

(*a*) by the oxidation of formaldehyde:

$$\text{H}-\overset{\displaystyle \text{H}}{\text{C}}=\text{O} \; + \text{O} \; = \; \text{H}-\overset{\displaystyle \text{OH}}{\text{C}}=\text{O}$$
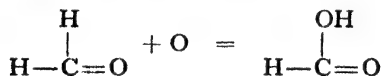
(*b*) by heating chloroform and iodoform with KOH:

$$\text{H}-\text{C}\diagup_{\text{Cl}}^{\text{Cl}}{\text{Cl}} + \text{KOH} \rightarrow \text{H}-\text{C}\diagup_{\text{OH}}^{\text{OH}}{\text{OH}} \rightarrow \text{H}-\text{C}\diagdown_{\text{O}}^{\text{OH}}$$
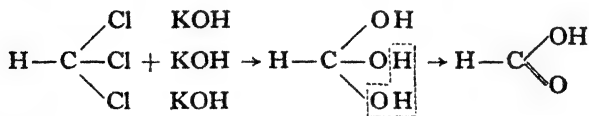
Acetic Acid, CH_3COOH or $C_2H_4O_2$.

Occurrence.—Acetic acid was known to the ancients in the form of wine vinegar. (The name " acid " is derived

from the Latin *acetum*, vinegar).   It is found either in the free state or as acetates in plant juices, milk, muscles, and perspiration, and in the excrement of animals.   Naturally occurring esters of acetic acid are also found; croton oil, for example, contains tri-acetin.

Formation.

1. By the atmospheric oxidation of alcohol or aldehyde in contact with platinum black:

$$C_2H_5OH + 2O = CH_3COOH + H_2O,$$
$$CH_3CHO + O = CH_3COOH.$$
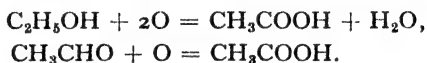
2. By gently heating sodium methoxide in an atmosphere of carbon monoxide at about 180° C., or by boiling methyl cyanide with alkalis or mineral acids:

$$CH_3ONa + CO = CH_3COONa,$$
$$CH_3CN + KOH + H_2O = CH_3COOK + NH_3.$$
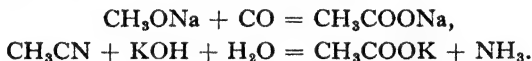
3. On the large scale by the destructive distillation of wood (p. 103).

When wood is distilled a brown aqueous distillate known as *pyroligneous acid* is obtained, which contains wood alcohol, acetone, and acetic acid.   By keeping the temperature comparatively low, the amount of acetic acid obtained is increased.

The distillate is neutralized with lime, the wood alcohol and acetone are distilled off, and the solution of crude calcium acetate thus obtained is evaporated to dryness to carbonize some of the impurities, and is then known as " grey acetate ". It is next treated with concentrated sulphuric acid or strong hydrochloric acid, and the acetic acid is distilled off under reduced pressure:

$$(CH_3COO)_2Ca + H_2SO_4 = CaSO_4 + 2CH_3COOH$$
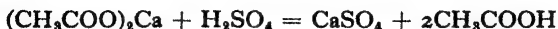
The crude acid, containing 80 per cent acetic acid, is fractionated in column stills and an acid containing 98·99 per

cent acetic acid is obtained. Chemically pure acetic acid is made from this by adding potassium permanganate or potassium dichromate to oxidize impurities, and distilling.

Glacial Acetic Acid is obtained by neutralizing with soda to form the sodium salt $(CH_3COO)Na \cdot 3H_2O$. This salt is then fused to expel the water of crystallization and distilled with concentrated sulphuric acid. The name is due to the fact that the anhydrous acid freezes readily in cold water (m. pt. 17°, b. pt. 118° C.).

4. By the acetous fermentation of alcoholic liquids.

Vinegar consists of a weak aqueous solution of acetic acid, together with other products e.g. ethyl acetate, which give it its aroma. It is prepared by the oxidation of alcoholic liquors. When beer and weak wine, such as claret, are exposed to air they become sour owing to the formation of this acid:

$$CH_3CH_2OH + O_2 = CH_3COOH + H_2O$$

This change is really a process of fermentation and not one of simple oxidation. It is brought about by acetic acid bacteria, of which several varieties exist, e.g. *Bacterium aceti*, *bacterium xylinium*, &c. These bacteria are present in the atmosphere and find their way into the liquors. They grow and multiply in alcoholic fluids which contain less than 15 per cent of alcohol; in addition, nitrogenous matter and salts are necessary for their nutrition. Hence alcoholic liquors like wine, beer and alcoholic mashes serve to propagate the bacteria, which convert the alcohol to vinegar. Strong wines like sherry and port, owing to their high alcoholic content, destroy the ferment; hence they do not turn sour and cannot be employed in the manufacture of vinegar. Pure alcohol also destroys the organism. *Bacterium aceti* occur as short rods (0·002 mm. in length) often attached together in chains.

Malt Vinegar is made by the French or Orleans process. Malt is first fermented in order to convert the starch into sugar. To the resulting liquid, called *wort*, yeast is added

to convert the sugar into alcohol. The alcoholic liquor is then converted into vinegar by the ferment, in aerated casks filled with beech shavings (see below). The vinegar so produced contains from 6 to 10 per cent of acetic acid; it is withdrawn periodically and fresh alcoholic liquor admitted.
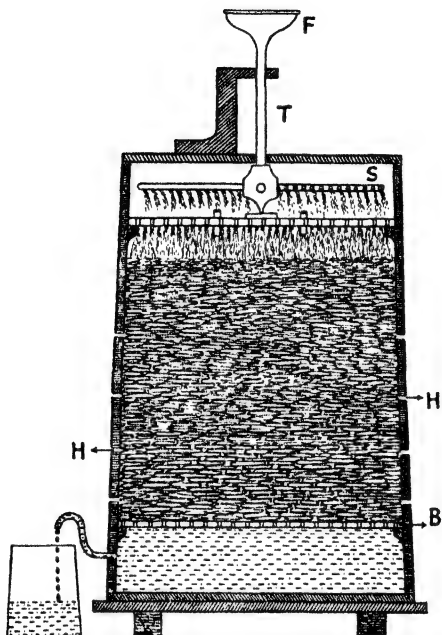
Fig. 26.—Manufacture of Vinegar. An Acetifier

Wine Vinegar is not manufactured in England, and is usually made on the Continent from wine of inferior quality by a process similar to that for malt vinegar. Its acetic acid content does not exceed 8 per cent.

The *Quick Vinegar* or *German Process* consists in allowing weak spirit containing 5 to 7 per cent of alcohol to run slowly over beech twigs or basket-work contained in an acetifier.

The *acetifier* (fig. 26) consists of a large wooden vat pro-

vided with a perforated false bottom B and numerous holes H in the sides for the admission of air.

The acetic acid bacterium (*Bacterium aceti*) is next developed by pouring strong vinegar over the wood and allowing it to stand for two days. The spirit called *gyle*, usually obtained from fermented wort, is then impregnated with *Bacterium aceti* and sprinkled over the basket-work by means of a rotating sparger S. The liquid is admitted into the funnel F, which is boxed in to prevent loss by evaporation. The liquid flows down the tube T and enters the sparger, which revolves on a pivot. In the arms of the sparger are a number of small holes through which the liquid flows, causing the sparger to revolve steadily and so sprinkle the basket-work. By the action of *Bacterium* or *Mycoderma aceti*, the alcohol is converted into vinegar. The best working temperature lies between 35° and 40° C. At this temperature the bacteria multiply most rapidly and hence the conversion to vinegar is most rapid. By means of a siphon arrangement, the vinegar is made to flow out continuously at the bottom; it is allowed to stand to develop its aroma and is finally clarified by filtration through fine sand or beechwood shavings.

It is essential that the aeration of the casks or vats should be carefully regulated. If too much air is admitted the alcohol is oxidized to carbon dioxide and water:

$$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O$$

whilst acetaldehyde is formed if the aeration is inadequate:

$$C_2H_5OH + O = CH_3CHO + H_2O$$
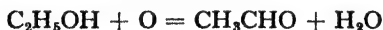
The vinegar produced by this process contains only 4 to 6 per cent of acetic acid. Vinegar cannot be used for the preparation of pure acetic acid.

5. Acetic acid was also manufactured on the large scale during the World War by the oxidation of acetaldehyde made from the hydration of acetylene in the presence

of mercury salts, and also by the oxidation of ethyl alcohol:

$$CH \equiv CH + HOH = CH_3 \cdot CHO,$$
$$CH_3CHO + O = CH_3 \cdot COOH.$$
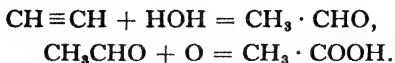
Properties.—Anhydrous acetic acid is a colourless, crystalline hygroscopic solid, m. pt. 17° C., b. pt. 118°, sp. gr. 1·055 at 15°. It has a pungent penetrating smell and a sharp sour taste. Its vapour burns with a blue flame. When acetic acid is mixed with water contraction takes place with increase in density, the maximum point corresponding to $CH_3C(OH)_3 = CH_3COOH \cdot HOH$ (ortho-acetic acid), which contains 77 per cent of acid. It is miscible with water, alcohol and ether in all proportions. It is an excellent solvent for most organic substances and for many inorganic substances, such as phosphorus, sulphur, iodine. Unlike formic acid, it has *no reducing properties.* It gives rise to painful wounds on tender parts of the skin. It is a fairly strong acid, dissolves certain metals, and acts readily on metallic hydroxides, carbonates, &c., producing salts called *acetates*; they are crystalline compounds, soluble in water and decomposed by mineral acids with liberation of acetic acid.

Uses.—In medicine for the preparation of synthetic remedies, e.g. aspirin, phenacetin; in the manufacture of synthetic dyes, e.g. synthetic indigo; in dyeing for the preparation of mordants, e.g. aluminium acetate. Calcium acetate is used in the manufacture of acetone.

Vinegar is used as a preservative and for curing meat and fish.

Tests for Acetic Acid and Acetates are given in Chap. XXII,

Constitution of Acetic Acid.

The molecular formula is $C_2H_4O_2$.

Sodium reacts with acetic acid, liberating hydrogen and forming sodium acetate:

$$C_2H_4O_2 + Na = C_2H_3O_2Na + H$$
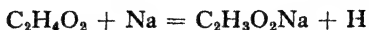
This reaction indicates that one hydrogen atom only is replaced and hence is not directly linked to a carbon atom.

Again, phosphorus pentachloride reacts with the acid to form acetyl chloride (p. 210); this reaction shows that an —OH group is present:

$$C_2H_4O_2 + PCl_5 = C_2H_3OCl + POCl_3 + HCl$$

The formula may therefore be written $C_2H_3O . OH$.

Again, when acetic acid is heated with sodium hydroxide methane is formed:

$$C_2H_3O \cdot OH + 2NaOH = CH_4 + Na_2CO_3 + H_2O$$

It is reasonable to assume that the methane must have been formed from that carbon atom which is attached to the greater number of hydrogen atoms.

Again, acetic acid contains a methyl or CH_3 group, as is shown by the fact that three of the four hydrogen atoms are displaceable by free chlorine to form *trichloracetic acid*, CCl_3COOH. The presence of the methyl group is also shown by the production of ethane on the electrolysis of potassium acetate:

$$
\begin{array}{l}
CH_3 \cdot COO\,K \\
 \\
CH_3 \cdot COO\,K
\end{array}
=
\begin{array}{l}
CH_3 \\
| \\
CH_3
\end{array}
+
\begin{array}{l}
CO_2 \\
 \\
CO_2
\end{array}
+ 2K
$$
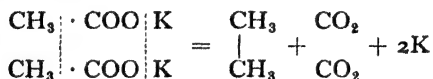
Acetic acid, therefore, must have the constitution

$$
\underset{\underset{H}{\displaystyle |}}{\overset{\overset{H}{\displaystyle |}}{H-C}}-\overset{\overset{OH}{\displaystyle |}}{C}=O \quad \text{or} \quad CH_3 \cdot CO \cdot OH
$$
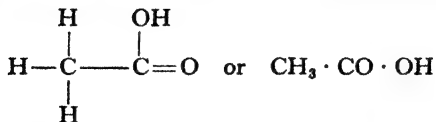
and must contain the carboxyl group —COOH.

Derivatives of Acetic Acid.

These include:

Sodium acetate	$CH_3 \cdot CO \cdot ONa$
Ethyl acetate	$CH_3 \cdot CO \cdot O \cdot CH_2 \cdot CH_3$
Acetic anhydride	$(CH_3CO)_2O$
Acetyl chloride	$CH_3 \cdot CO \cdot Cl$
Thio-acetic acid	$CH_3 \cdot CO \cdot SH$
Acetamide	$CH_3 \cdot CO \cdot NH_2$

We shall discuss acetamide, acetic anhydride, and acetyl chloride as typical members of the class of compounds to which they belong.

Amides.

An **amide** is the compound derived from the acid by the introduction of the **amido** $-NH_2$ group in place of the hydroxyl radicle of the carboxyl group,

$$R \cdot CO \cdot OH \to R \cdot CO \cdot NH_2 \, (R = C_nH_{2n+1});$$
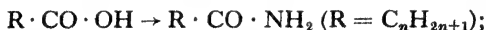
e.g.   Formamide $H \cdot CO \cdot NH_2$,
        Acetamide $CH_3 \cdot CO \cdot NH_2$.

The $-NH_2$ group is usually termed an **amino** group when present in a primary amine but an **amido** group when present in an acid amide.

Tests for Amides are given in Chap. XXV, p. 563.

Acetamide, Ethane amide, CH_3CONH_2.

Formation.

1. By slowly distilling ammonium acetate in a stream of dry ammonia:

$$CH_3CO \cdot ONH_4 = CH_3CO \cdot NH_2 + H_2O$$

Experiment.—Weigh out into a 500 c.c. distilling flask 45 gm. of ammonium acetate and then add 55 c.c. of glacial acetic acid. Fit the flask to a reflux condenser, closing the exit tube of the flask by means of rubber tubing and

glass rod. Gently boil the mixture on a sand bath for 4–5 hours. Disconnect the reflux, insert a thermometer, and connect the exit tube to a long wide air condenser. On distillation, ammonia, water and acetic acid distil first. When the temperature reaches 200° C., change the receiver; the distillate which now collects solidifies and consists mainly of acetamide.

2. By heating ethyl acetate with concentrated aqueous ammonia under pressure:

$$CH_3CO \cdot OC_2H_5 + NH_3 = CH_3CO \cdot NH_2 + C_2H_5OH$$
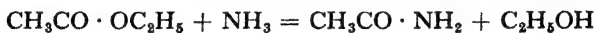
3. By treating acetyl chloride (p. 210) with ammonia:

$$CH_3COCl + 2NH_3 = CH_3CONH_2 + NH_4Cl$$
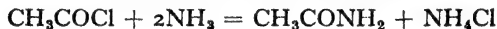
4. By the addition of water to the alkyl cyanide (nitrile):

$$CH_3CN + H_2O = CH_3CONH_2$$
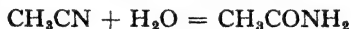
This addition of water is frequently effected by dissolving the nitrile in concentrated sulphuric acid or in a mixture of acetic and concentrated sulphuric acids or by shaking with cold concentrated hydrochloric acid; also, often quantitatively, by hydrogen peroxide in alkaline solution.

Properties.—Colourless crystalline needles, m. pt. 81° C., b. pt. 222° C. When pure it has only a faint odour, but usually it has a strong smell of mice, owing to traces of impurity: it is readily soluble in water and in alcohol.

Reactions.

1. It reacts with a strong base to form a salt, with liberation of ammonia:

$$CH_3CONH_2 + KOH = CH_3COOK + NH_3$$
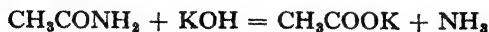
2. Dehydrating agents, e.g. P_2O_5, convert it into methyl cyanide (acetonitrile):

$$CH_3CO \cdot NH_2 - H_2O = CH_3CN$$

3. It is hydrolysed by concentrated hydrochloric acid or moderately concentrated sulphuric acid:

$$CH_3CO \cdot NH_2 + HOH = CH_3COOH + NH_3$$
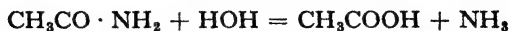
From these reactions we see that three classes of compounds, namely, the ammonium salts of the acids, the amides, and the cyanides are inter-related, as methyl cyanide on hydrolysis can be converted into acetic acid and ammonia and on partial hydrolysis into acetamide:

$$CH_3COONH_4 \rightleftharpoons CH_3CONH_2$$
$$CH_3CN$$
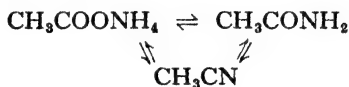
4. It forms unstable additive compounds with some acids, e.g. acetamide hydrochloride, $(CH_3CO\ NH_2)_2 . HCl$.

5. (*Hofmann's reaction.*) When an acid amide is treated with bromine in an excess of sodium or potassium hydroxide, the first product is acetobromamide (cf. p. 147):

$$CH_3CONH_2 + Br_2 = CH_3CONHBr + HBr.$$
Acetamide   Acetobromamide
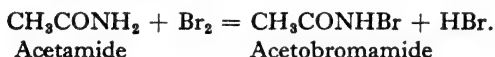
Sodium hydroxide reacts with acetobromamide (which has acid properties, owing to the presence of the carbonyl group and the bromine atom) to form a salt $CH_3CONa\ N\ Br$, which is unstable, undergoing molecular rearrangement:

$$\begin{array}{ccccc}
CH_3C-O-Na & & Br-C-O-Na & & \\
\parallel & \rightarrow & \parallel & \rightarrow & CH_3-N{=}C{=}O \\
N-Br & & N-CH_3 & & \\
\text{Sodium aceto-} & & \text{Intermediate} & & \text{Methyl} \\
\text{bromamide} & & \text{product} & & \text{isocyanate}
\end{array}$$
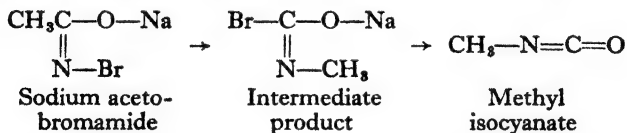
The methyl isocyanate formed reacts in the presence of the alkali to give the primary amine and carbon dioxide, which reacts with the sodium hydroxide to form sodium carbonate:

$$CH_3NCO + 2NaOH = CH_3NH_2 + Na_2CO_3$$
or $$CH_3CONHBr + 3NaOH = CH_3NH_2 + Na_2CO_3 + NaBr + H_2O.$$
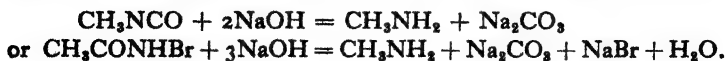
It is thus possible to pass from the acid to the primary amine containing the same hydrocarbon radicle as the acid or containing one carbon atom less than the original amide:

$$CH_3COOH \rightarrow CH_3CONH_2 \rightarrow CH_3NH_2$$

Acetic acid   Acetamide   Methylamine

6. It reacts with nitrous acid to form acetic acid and nitrogen:

$$\begin{array}{c} CH_3CO \mid N \mid H_2 \\ + OH \mid N \mid O \end{array} = CH_3COOH + N_2 + H_2O$$
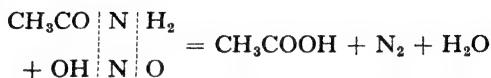
Formamide, Methane amide, $H \cdot CO \cdot NH_2$, is a liquid readily soluble in water and alcohol. It boils at 200° C. with partial decomposition. When quickly heated it decomposes into CO and NH_3, and with phosphorus pentoxide it yields hydrocyanic acid.

Constitution of Acetamide.

The constitutional formula of acetamide may be either

$$(I)\ CH_3-C\!\!\begin{array}{c}\diagup O\\[-2pt]\diagdown NH_2\end{array} \quad or \quad (II)\ CH_3-C\!\!\begin{array}{c}\diagup OH\\[-2pt]\diagdown NH\end{array}$$
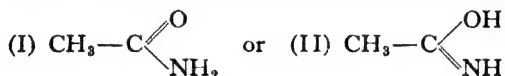
Formula (I) is supported by its methods of formation and its properties. Formula (II) passes easily into the first by the migration of a hydrogen atom, and most of the reactions of the simple amides are explained almost equally well by either formula. This compound thus appears to possess two distinct formulæ (an example of a **tautomeric** substance), and gives rise to two distinct alkyl derivatives:

$$CH_3-C\!\!\begin{array}{c}\diagup O\\[-2pt]\diagdown NH\,C_2H_5\end{array} \quad and \quad CH_3-C\!\!\begin{array}{c}\diagup OC_2H_5\\[-2pt]\diagdown NH\end{array}$$
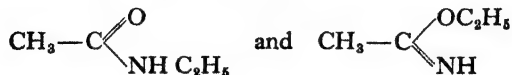
which are isomeric but differ in physical and chemical properties. The first closely resembles the original amide;

the second differs considerably from it and is usually known as an **imino ether**.

The above remarks apply to the acid amides in general.

A tautomeric compound may be defined as a compound which can react with other substances in such a way that it appears to be a compound with two different constitutional formulae.

Tautomerism (from ταὐτο (*tauto*), the same; μέρος (*meros*), a part) **is the phenomenon exhibited by a tautomeric compound.**

Examples of Tautomerism.

Hydrogen cyanide	$H \cdot N = C \rightleftharpoons H \cdot N \equiv C \rightleftharpoons N \equiv C \cdot H$
Ethyl aceto-acetate	$CH_3COCH_2COOC_2H_5$
	$\rightleftharpoons CH_3C(OH) = CHCOOC_2H_5$
Nitro-ethane	$CH_3 \cdot CH_2NO_2 \rightleftharpoons CH_3 \cdot CH = NO \cdot OH$
Cyanic acid	$HO - CN \rightleftharpoons HN = C = O$
Sulphurous acid	$SO_2\begin{smallmatrix} \diagup H \\ \diagdown OH \end{smallmatrix} \rightleftharpoons O = S\begin{smallmatrix} \diagup OH \\ \diagdown OH \end{smallmatrix}$

Acetic Anhydride, $(CH_3CO)_2O$.

This compound is produced by distilling a mixture of sodium acetate and acetyl chloride (see below):

$$\begin{array}{c} CH_3COO - \fbox{Na} \\ + \\ CH_3CO \quad - \fbox{Cl} \end{array} = \begin{array}{c} CH_3CO \\ \\ CH_3CO \end{array}\!\!\!\diagdown\!\!\!\diagup O + NaCl$$
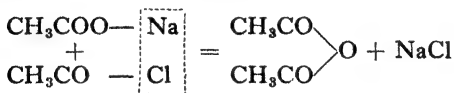
It is a pungent liquid, b. pt. 137° C. It is used as an *acetylating agent*:

$$\begin{array}{c} CH_3CO \\ \\ CH_3CO \end{array}\!\!\!\diagdown\!\!\!\diagup O + C_2H_5OH = \begin{array}{c} CH_3CO \\ \\ C_2H_5 \end{array}\!\!\!\diagdown\!\!\!\diagup O + CH_3COOH$$

| Acetic anhydride | Ethyl acetate | Acetic acid |
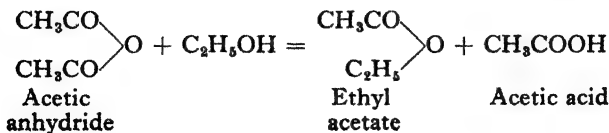
Acetyl Chloride, CH_3COCl.

Formation.—1. By adding phosphorus trichloride slowly to glacial acetic acid contained in a distilling flask connected to a Liebig condenser. When the phosphorus trichloride has all been added the mixture is distilled from the water bath:

$$3CH_3COOH + 2PCl_3 + 3H_2O = 3CH_3COCl + 2H_3PO_3 + 3HCl$$

The reaction takes place in stages; hydrogen chloride is formed and the phosphorous oxide then reacts with the water present to form phosphorous acid. The distillation should be conducted in a fume cupboard or the receiver connected with a soda-lime tower to absorb the hydrogen chloride:

$$3CH_3COOH + 2PCl_3 = 3CH_3COCl + 3HCl + P_2O_3,$$
$$P_2O_3 + 3HOH = 2H_3PO_3.$$
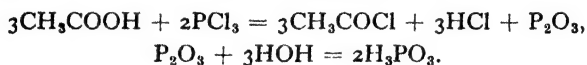
2. Phosphorus pentachloride reacts with acetic acid to form acetyl chloride and phosphorus oxychloride:

$$CH_3COOH + PCl_5 = CH_3COCl + HCl + POCl_3$$

Acetyl chloride is a colourless fuming liquid, b. pt. 55° C.

Reactions.—1. It is rapidly hydrolysed by water:

$$CH_3CO\,|\,Cl + H\,|\,OH = CH_3COOH + HCl$$
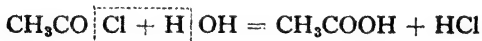
2. It forms ethyl acetate with ethyl alcohol:

$$CH_3CO\,|\,Cl + H\,|\,OC_2H_5 = CH_3COOC_2H_5 + HCl$$
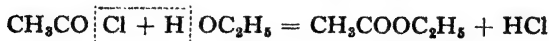
This reaction is of considerable importance as a means of detecting the presence of hydroxyl groups: the hydroxyl —OH group is converted into an **acetoxyl** $-O\,.\,CO\,.\,CH_3$ group.

3. It forms acetamide with ammonia or ammonium carbonate:

$$CH_3CO \cdot Cl + 2NH_3 = NH_4Cl + CH_3CO \cdot NH_2$$
$$\text{Acetamide}$$
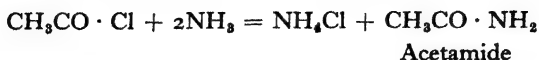
and acetanilide with aniline:

$$CH_3COCl + C_6H_5NH_2 = C_6H_5NHCOCH_3 + HCl$$
$$\text{Aniline} \qquad \text{Acetanilide}$$
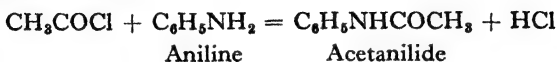
These reactions are employed as a means of introducing an **acetyl** $CH_3 . CO-$ radicle in place of hydrogen (a) in any alcohol, (b) in ammonia or any derivative of ammonia which still has a hydrogen atom attached to a nitrogen atom.

Propionic Acid, C_2H_5COOH.

Occurrence.—In pyroligneous acid.

· *Formation.*—1. By oxidation of propyl alcohol with potassium dichromate and sulphuric acid:

$$C_2H_5 \cdot CH_2OH + 2O = C_2H_5COOH + H_2O$$
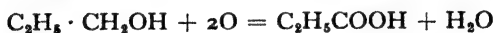
2. By hydrolysis of ethyl cyanide (propionitrile) by alkalis:

$$C_2H_5CN + 2H_2O = C_2H_5COOH + NH_3$$
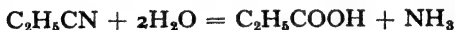
3. By *Schizomycetes* fermentation of calcium lactate or calcium malate, $Ca(C_4H_4O_5)$.

4. By the action of carbon dioxide on sodium ethyl,

$$CO_2 + C_2H_5Na = C_2H_5COONa,$$
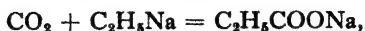
followed by treatment of the sodium salt with sulphuric acid and distillation of the acid set free.

5. By reduction of acrylic acid or lactic acid.

(A) *Direct reduction* by hydriodic acid and phosphorus, or

sodium amalgam and water, or hydrogen and reduced nickel at 100° C.:

$$H-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-\underset{}{\overset{O}{\overset{\|}{C}}}-OH + 2H = H-\underset{\underset{H}{|}}{\overset{H}{\overset{|}{C}}}-\underset{\underset{H}{|}}{\overset{H}{\overset{|}{C}}}-COOH$$

  Acrylic acid
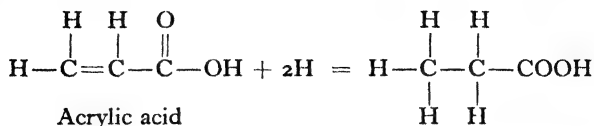
(B) *Indirect reduction* by heating with concentrated hydriodic acid. The reaction takes place in two stages, as follows:

(a) $CH_3CHOH \cdot COOH + HI = CH_3CHI \cdot COOH + H_2O$,
  Lactic acid

(b) $CH_3CHI \cdot COOH + HI \quad = CH_3CH_2COOH + I_2$.
  α-iodolactic acid
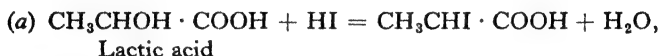
Properties.—Propionic acid is an oily liquid, m. pt. —36° C., b. pt. 141° C. It has a pungent sour smell. It dissolves in water but can be separated from its aqueous solution by the addition of calcium chloride. It forms an oily layer on the surface, hence the name *propionic*, from πρῶτος (*protos*), first and πιων (*pion*), fat. It is a monobasic acid and forms salts known as *propionates*.

Butyric Acid, C_3H_7COOH, is found in pyroligneous acid. It exists in two isomeric forms.

(A) **Normal Butyric Acid,** $CH_3CH_2CH_2 \cdot COOH$, occurs in perspiration, in the large intestine, in certain secretions and in the juice of flesh. It is also found to the extent of 2 to 3 per cent in butter as the glyceride (glyceryl ester). It is also found in the fruit of certain plants, e.g. *Pastinaca sativa, Heracleum giganteum.* Rancid butter probably contains the free acid.

Formation.—1. By the oxidation of normal butyl alcohol.

2. By the hydrolysis of normal propyl cyanide by alkalis:

$$CH_3CH_2CH_2CN + 2HOH = CH_3CH_2CH_2COOH + NH_3$$
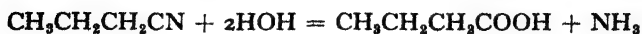
3. By " butyric fermentation " of sugar, starch, and other carbohydrates by the combined action of lactic ferment and *Bacillus subtilis* or *boocapricus*. The acid formed during the fermentation is neutralized by either calcium or zinc carbonate, otherwise the acid would arrest the fermentation process. The fermentation may be started by decaying cheese, although now pure cultures of butyric acid bacteria are employed; the temperature of the reaction is kept at about 30° C.

The glucose is first converted into lactic acid, which is then decomposed into butyric acid as follows:

$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHO \end{array} = \begin{array}{c} CH_3 \cdot CHOH \cdot COOH \\ + \\ CH_3 \cdot CHOH \cdot COOH \end{array} = CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$$

Glucose   Lactic acid   Butyric acid
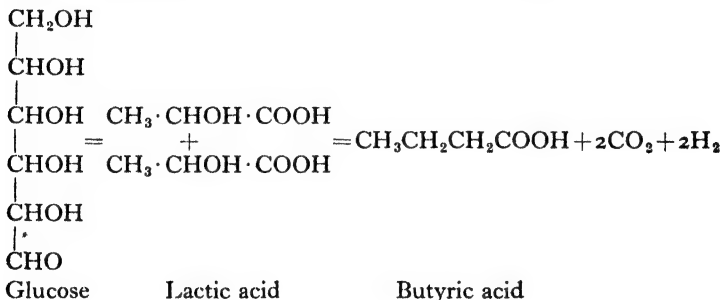
Acetic, caproic, and caprylic acids are, however, formed at the same time, but only to a small extent.

To the solution which contains the acid as either the calcium or the zinc salt, sodium carbonate is added. This precipitates the metal as the insoluble carbonate. The precipitate is filtered off and the filtrate containing sodium butyrate is treated with sulphuric acid, when the acid is liberated: it is then recovered by fractional distillation.

Properties.—Thick sour liquid, m. pt. −8° C., b. pt. 163°, sp. gr. 0·978. The liquid smells of rancid butter and of perspiration. It is miscible with water and separates from the aqueous solution on the addition of mineral salts. It forms salts known as *butyrates*. Calcium butyrate is more soluble in cold water than in hot water; the dissolving of this salt is accompanied by a slight increase in temperature.

Uses.—In the manufacture of certain alkyl salts and commercial fruit essences, such as those of apricot, strawberry, and peach.

(B) **Isobutyric Acid,** $(CH_3)_2CHCOOH$, occurs in the root of *Arnica montana* and as esters in Roman camomile oil and in many plants.

Formation.—1. By the oxidation of isobutyl alcohol:

$$\begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} CH \cdot CH_2OH + 2O = \begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} CH \cdot COOH + H_2O$$
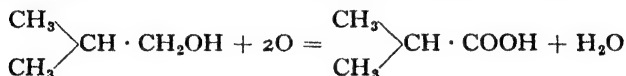
2. By the hydrolysis of isopropyl cyanide by alkalis:

$$\begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} CH \cdot CN + 2HOH = \begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} CH \cdot COOH + NH_3$$
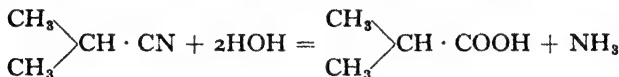
3. By aceto-acetic ester synthesis (p. 137).

Properties.—Similar to those of the normal acid, but it is less soluble in water; b. pt. $155.5°$ C. It is easily oxidized to acetone or acetic acid and carbon dioxide:

$$\begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} CH \cdot COOH + O_2 = \begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} CO + CO_2 + H_2O$$
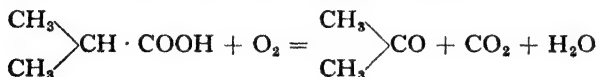
It forms salts (*isobutyrates*). The calcium salt is more soluble in hot water than in cold water: the dissolving of this salt is accompanied by a slight absorption of heat (contrast the normal salt: this serves as a means of separation).

Nomenclature

I. In the various acids of the open-chain order such as

A. Propionic acid $\overset{\beta}{C}H_3 - \overset{\alpha}{C}H_2 - COOH$
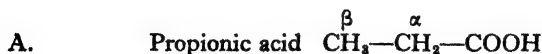
it is usual to refer to the carbon atoms in the chain by the letters of the Greek alphabet. The carbon atom next to the carboxyl group is known as the alpha (α) carbon atom,

the second as the beta (β), the third as the gamma (γ), the fourth as the delta (δ), and so on.

Propionic acid, however, may be regarded as acetic acid in which one hydrogen atom in the α-position has been replaced by one methyl group. Propionic acid is therefore *methyl acetic acid*. By substituting one chlorine atom for one hydrogen atom, excluding the H atom of the carboxyl group in every case, the following substituted acids are obtained:

$CH_3 \cdot \mathbf{C}HCl \cdot COOH$ is α-chloropropionic acid (b. pt. 186° C.),

$CH_2Cl \cdot CH_2 \cdot COOH$ is β-chloropropionic acid (b. pt. 204° C.).

It will be observed that the α-substitution product contains an asymmetric carbon atom (p. 255), indicated by black type, while the β-product does not.

B.   Normal butyric acid $\overset{\gamma}{C}H_3 — \overset{\beta}{C}H_2 — \overset{\alpha}{C}H_2 — COOH$

This acid may also be regarded as:

(*a*) Acetic acid in which one hydrogen atom of the $—CH_3$ group has been replaced by an ethyl group.

Butyric acid is therefore *ethyl acetic acid*.

(*b*) Propionic acid in which one hydrogen atom in the β-position has been replaced by a methyl group.

Butyric acid is therefore β-*methyl propionic acid*.

By substituting chlorine as already described the following substituted acids may be obtained:

$CH_3 \cdot CH_2 \cdot \mathbf{C}HCl \cdot COOH$ is α-chlorobutyric acid

$CH_3 \cdot \mathbf{C}HCl \cdot CH_2 \cdot COOH$ is β-chlorobutyric acid

$CH_2Cl \cdot CH_2 \cdot CH_2 \cdot COOH$ is γ-chlorobutyric acid

For Practice.—Name the compounds which should be produced when one hydrogen atom in each of the following acids is

substituted by one of the following radicles: Br, I, OH, CN, SO_3H (sulpho)·

(*a*) acetic acid, (*b*) propionic acid, (*c*) butyric acid.

II. In the various acids of the branched-chain order such as

$$\text{Isobutyric acid} \quad \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} \Big> CH \cdot COOH$$
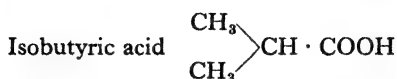
a difficulty presents itself as to the Greek lettering of the carbon atoms.

Isobutyric acid may be regarded as:

(*a*) Acetic acid in which two hydrogen atoms of the —CH_3 group have been replaced by two methyl groups.

It is therefore *Dimethyl acetic acid*.

(*b*) Propionic acid in which one hydrogen atom in the α-position has been replaced by a methyl group.

It is therefore α-*methyl propionic acid*.

By substituting chlorine as already described the following isomeric acids may be obtained:

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} \Big> CCl \cdot COOH \text{ is α-chloro-isobutyric acid,}$$

$$\begin{matrix} CH_2Cl \\ \\ CH_3 \end{matrix} \Big> CH \cdot COOH \text{ is β-chloro-isobutyric acid,}$$

or, otherwise expressed,
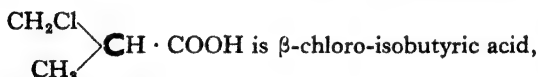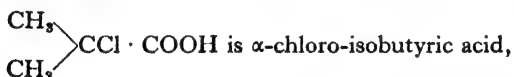
$$\overset{\beta}{CH_2}Cl \cdot \overset{\alpha}{C}H \cdot COOH$$
$$\quad | $$
$$\quad CH_3 \qquad \text{is α-methyl-β-chloropropionic acid.}$$
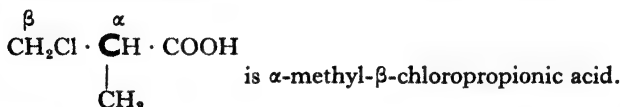
Further, the branch-chain may contain different *alkyl* groups, e.g.

$$\text{Active valeric acid} \quad \begin{matrix} CH_3 \cdot CH_2 \\ \\ CH_3 \end{matrix} \Big> CH \cdot COOH$$
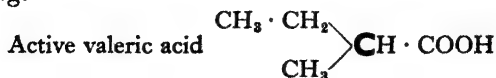
Regarding this compound as a methyl derivative of butyric acid, we may letter the formula as follows:

$$\overset{\gamma}{CH_3} \cdot \overset{\beta}{CH_2} \ \overset{\alpha}{\mathbf{C}H} \cdot COOH$$
$$\underset{CH_3}{|}$$

, i.e. α-methyl butyric acid
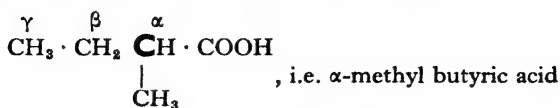
But this acid may also be regarded as an ethyl derivative of propionic acid:

$$\overset{\beta}{CH_3} \cdot \overset{\alpha}{\mathbf{C}H} \cdot COOH$$
$$\underset{C_2H_5}{|}$$

, i.e. α-ethyl propionic acid,
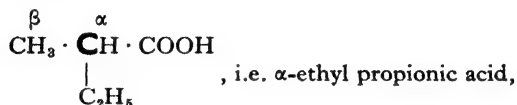
and also as a derivative of acetic acid:

$$CH_3$$
$$|$$
$$\mathbf{C}H—COOH, \text{ i.e. methyl ethyl acetic acid,}$$
$$|$$
$$C_2H_5$$
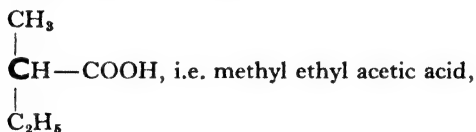
There are three " active " valeric acids, one dextro-rotatory, one lævo-rotatory, and one optically inactive (see pp. 257, 264):

SUBSTANCES DERIVED FROM ETHYL ALCOHOL

ETHYL ALCOHOL
CH_3CH_2OH

Dehydrate with P_2O_5

ETHYLENE $CH_2 = CH_2$

Reduce → **ETHANE** $CH_3 \cdot CH_3$

Br_2 → **ETHYLENE BROMIDE** $CH_2Br \cdot CH_2Br$

Potash → **ACETYLENE** $CH \equiv CH$

ACETALDEHYDE $CH_3CHO \leftarrow H_2O$—

$2HCl$ → **ETHYLENE DICHLORIDE** $CH_2Cl \cdot CH_2Cl$

Reduction → **ETHYL ALCOHOL**

KCN → **ETHYLENE DICYANIDE** $CH_2CN \cdot CH_2CN$

Hydrolysis → **SUCCINIC ACID** CH_2COOH CH_2COOH

HCl → **ETHYL CHLORIDE** CH_3CH_2Cl ←Cl—**ETHANE**

Ammonia → **ETHYLAMINE** $CH_3CH_2NH_2$

Oxidation → **ACETALDEHYDE** CH_3CHO

Oxidation → **ACETIC ACID** $CH_3 \cdot COOH$

Distil Ammonium Salt

Sodium Salt + Soda Lime → **METHANE** CH_4

Cl_3 → **METHYL CHLORIDE** CH_3Cl — Ammonia → **METHYLAMINE** CH_3NH_2 NH_3

PCl_3 → **ACETYL CHLORIDE** CH_3COCl

Ammonia → **ACETAMIDE** CH_3CONH_2

Bromine + KOH → **METHYL CYANIDE** (Acetonitrile) CH_3CN

Dehydrate with H_2SO_4 → **ETHER** $C_2H_5 \cdot O \cdot C_2H_5$

Ethyl Alcohol

ETHYL ACETATE $CH_3CO \cdot OC_2H_5$

Hydrolysis

ETHYL ACETO-ACETATE $CH_3COCH_2COOC_2H_5$

Ketonic Hydrolysis | Acid Hydrolysis

ACETONE CH_3COCH_3 | **ACETIC ACID**

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ACIDS DERIVED FROM ACETIC ACID

ACETIC ACID
CH_3COOH

Right branch — Distil Ca Salt with Ca formate →

Acetaldehyde CH_3CHO
— HCN →
Cyanhydrin $CH_3CH(OH)CN$
— Hydrolysis →
LACTIC ACID $CH_3CH(OH)\cdot COOH$
— Butyric Bacillus →
BUTYRIC ACID $CH_3CH_2CH_2COOH$

Centre branch — Cl_2 →

MONOCHLORACETIC ACID $CH_2Cl\cdot COOH$

- KOH → **GLYCOLLIC ACID** $CH_2OH\cdot COOH$

- KCN → **CYANO-ACETIC ACID** $CH_2CN\cdot COOH$
  — Hydrolysis →
  MALONIC ACID $CH_2(COOH)(COOH)$
  — Sodium →
  $NaCH(COOH)(COOH)$
  — CH_3I →
  $CH_3CH(COOH)(COOH)$
  — Heat →
  PROPIONIC ACID CH_3CH_2COOH

- Na → **SUCCINIC ACID** $CH_2COOH\;\; CH_2COOH$

Left branch — Distil Ca Salt →

Acetone CH_3COCH_3
— Bleaching Powder →
Chloroform $CHCl_3$
— Alcoholic KOH with HCl →
FORMIC ACID $H\cdot COOH$
— Heat Na Salt; treat residue with H_2SO_4 →
OXALIC ACID $COOH\;\; COOH$

QUESTIONS

1. What is an organic acid? Indicate two methods by which these substances can be prepared and describe how they react with (*a*) phosphorus pentachloride, (*b*) caustic soda, (*c*) methyl alcohol.   (*Higher School Cert.*)

2. Starting with acetic acid, how would you prepare: (*a*) acetone, (*b*) propionic acid, (*c*) acetic aldehyde, (*d*) methane?

3. Outline the preparation in as pure a state as possible of (*a*) methylamine, (*b*) acetamide. Compare and contrast the reactions (if any) of methylamine, dimethylamine, and acetamide with sodium hydroxide, methyl iodide, and nitrous acid.

                    (*Inter. B. Pharm., London.*)

4. What do you understand by (*a*) an ester, (*b*) an acid amide? By what characteristics can esters and acid amides respectively be recognized? How may the ethyl ester and the amide of acetic acid be prepared?

5. What do you understand by the term " homologous series "? Illustrate your answer by a brief description of the chemical and physical properties of the fatty acids.

                    (*Chemists and Druggists Qual.*)

6. Show, by means of properly balanced equations, how the following cycle of changes may be effected:

Acetamide → methylamine → methyl alcohol → methyl iodide → acetonitrile → acetic acid → acetamide.

State briefly the conditions under which each action will take place.   (*Civil Service: Executive Group.*)

7. How is formic acid prepared? Give its constitutional formula and state on what evidence it rests. What is the effect of heating formic acid with (*a*) strong sulphuric acid, (*b*) litharge, (*c*) ethyl alcohol, (*d*) a solution of potassium permanganate in dilute sulphuric acid?   (*Inter B.Sc. Eng.*)

8. Describe one method by which acetic acid is obtained commercially.

Upon what evidence is the formula CH_3COOH assigned to this compound?   (*Civil Service: Executive Group.*)

9. Give as many methods as you can—with examples—for the preparation of amides.

What changes take place when acetamide is heated with (*a*) phosphorus pentoxide, (*b*) sodium hydroxide solution?

10. State in detail the complete evidence required to establish the constitution of acetic acid. (*Inter. B.Pharm., London.*)

11. How do the following substances react together:
    (*a*) ethylene and sulphuric acid;
    (*b*) acetylene and ammoniacal silver nitrate;
    (*c*) acetamide and phosphorus pentoxide;
    (*d*) ethyl alcohol, phosphorus and iodine?

12. How may pure acetic acid be obtained, starting from (*a*) a dilute solution of the acid, and (*b*) acetylene? What products are formed on heating calcium acetate (*a*) alone, (*b*) with calcium formate? (*II. M.B., London.*)

13. State the evidence on which the accepted constitution of acetic acid is based. How may acetic acid be converted into (*a*) ethyl acetate, and (*b*) acetone? (*Inter. B.Sc., Eng.*)

14. How does phosphorus pentachloride react with each of the following: ethyl alcohol, diethyl ether, acetic acid, acetaldehyde?

15. Describe a method for the preparation of (*a*) ethyl chloride, (*b*) acetyl chloride. Compare and contrast the physical and chemical properties of these substances.

(*Chemists and Druggists Qual.*)

16. Show by graphic or structural formulæ the relationship of acetic acid to its chloride, anhydride, and amide.

Indicate briefly how each of these derivatives may be prepared from acetic acid.

17. Give two methods for the preparation of acetic acid. How may it be converted into (*a*) acetyl chloride, (*b*) acetic anhydride, (*c*) acetamide, (*d*) methyl cyanide?

(*Chemists and Druggists Qual.*)

18. Starting with acetic acid, how would you prepare the following: acetyl chloride, acetic anhydride, acetamide? By what

general methods are esters of organic acids prepared? Illustrate your answer by reference to the preparation of ethyl acetate.

19. How is acetic acid obtained on the large scale? Mention any reactions which support the formula assigned to this acid. Describe shortly the preparation of an ester of acetic acid.

(Inter. B.Sc. Eng.)

20. How can acetamide be obtained from ethylamine? What are the chief properties of these two substances?

21. How would you prepare (*a*) monochloracetic acid, (*b*) acetyl chloride?

Describe the chief properties and reactions of the two substances.   *(Phar. Chem. Qual.)*

22. What is pyroligneous acid, and how is it obtained? How could pure specimens of the following: (*a*) methyl alcohol, (*b*) acetic acid, (*c*) acetone, be isolated from pyroligneous acid?

23. Give the full structural formulæ for acetic anhydride and acetyl chloride. What is the action of acetyl chloride on (*a*) sodium acetate, (*b*) alcohol, (*c*) aniline, (*d*) water?

24. Describe either how methyl alcohol and acetic acid are obtained from wood or how ethyl alcohol is obtained on the large scale. Describe the effect of heat on (*a*) calcium acetate, (*b*) ammonium acetate.   *(Oxford Higher School Cert.)*

25. The wood distillation industry has been ruined by the recent introduction of synthetic methods for the preparation of acetic acid and methyl alcohol.

Comment on this statement.

Describe these modern methods for the preparation of methyl alcohol or acetic acid.   *(Cambridge Higher School Cert.)*

26. Give an account of the manufacture of acetic acid from calcium carbide. From what other sources can acetic acid be obtained? Mention the uses of this acid.

(Cambridge Higher School Cert.)

Fats and Oils: Polyhydric Alcohols

Most animal and vegetable fats and oils, e.g. suet, tallow, butter, palm oil, olive oil, and seal oil consist almost entirely of so-called *glycerides*. The nature of these substances was elucidated by Chevreul in 1811, who showed that they are compounds of fatty acids with glycerol (p. 234). The fatty acids found in fats are mainly:

<div align="center">

Palmitic, $C_{15}H_{31}COOH$ ⎫

Stearic, $C_{17}H_{35}COOH$ ⎬ Saturated acids

Oleic, $C_{17}H_{33}COOH$ Unsaturated acid

</div>

The glyceryl esters or glycerides of these acids are termed respectively:

<div align="center">

Tripalmitin, $C_3H_5(O \cdot CO \cdot C_{15}H_{31})_3$, a solid

Tristearin, $C_3H_5(O \cdot CO \cdot C_{17}H_{35})_3$, a solid

Tri-olein, $C_3H_5(O \cdot CO \cdot C_{17}H_{33})_3$, a liquid

</div>

The consistency of a fat or oil depends on the relative amount of the solid esters present. When a fat contains a relatively large proportion of tristearin and tripalmitin it is solid and comparatively hard, e.g. *tallow*; when, however, it contains a relatively large proportion of tri-olein it is soft and pasty (*lard*) or liquid (*olive oil*).

Oleic acid is an unsaturated fatty acid, since it contains two atoms of hydrogen less than stearic acid. On account

of its association with the glycerides of the saturated fatty acids in oils and fats, it is included here for convenience.

The constitutional formula of tristearin (glyceryl stearate) may be represented as follows:

$$C_{17}H_{35}CO \cdot O—CH_2$$
$$C_{17}H_{35}CO \cdot O—CH$$
$$C_{17}H_{35}CO \cdot O—CH_2$$
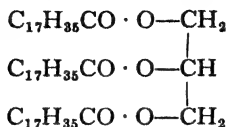
These glycerides can be formed directly by the action of glycerol with the fatty acid.

Glycerol is a tri-acid base and hence can combine with and neutralize three molecules of a monobasic or mono-carboxylic acid, forming neutral salts, e.g.:

$$CH_2 \cdot OH + HO \cdot CO \cdot C_{17}H_{35} \qquad CH_2 \cdot O \cdot CO \ C_{17}H_{35}$$
$$CH \cdot OH + HO \cdot CO \cdot C_{17}H_{35} = CH \cdot O \cdot CO \ C_{17}H_{35} + 3HOH$$
$$CH_2 \cdot OH + HO \cdot CO \cdot C_{17}H_{35} \qquad CH_2 \cdot O \cdot CO \cdot C_{17}H_{35}$$

Glycerol   Stearic acid   Tristearin
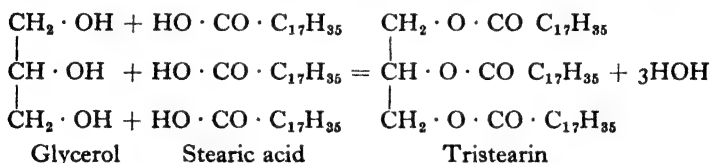
These glycerides, like other esters, are decomposed by water and by dilute mineral acids at moderately high temperatures, being converted into glycerol and an acid; in the case of tripalmitin, for example, palmitic acid is formed:

$$C_3H_5(O \cdot CO \cdot C_{15}H_{31})_3 + 3HOH$$
$$= C_3H_5(OH)_3 + 3C_{15}H_{31}COOH$$
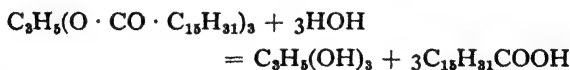
Since fats and oils are mixtures of glycerides they yield mixtures of fatty acids on hydrolysis (saponification).

Analysis of Oils and Fats.

The analysis of oils and fats is of great technical importance.

Two important values are always determined in the analysis of oils and fats:

I. The Saponification Value (Koettstorfer Number).

II. The Iodine Value.

I. The **saponification value** is the amount of alkali required to neutralize the fatty acids in a given weight of oil or fat. A weighed quantity of the fat or oil is heated with excess of a standard solution of alcoholic potash. The amount of alkali required to neutralize the fatty acids is found by subsequently titrating the excess of alkali with standard hydrochloric acid.

The saponification value is expressed as the number of milligrams of potassium hydroxide required to saponify one gram of fat or oil. For example,

2·0676 gm. of olive oil required 14·9 c.c. of N/2 KOH ($f = 0·973$).

Saponification value $= 14·9 \times \dfrac{0·973}{2·068} \times 0·028 \times 1000$
$$= 196.$$

II. The **iodine value** or the amount of iodine chloride absorbed gives a measure of the amount of unsaturated acids present, since these substances possess the property of forming additive compounds with iodine chloride quantitatively. For example,

$$C_{17}H_{33}COOH + ICl = C_{17}H_{33}ICl \cdot COOH$$
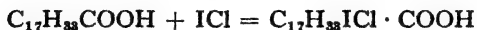
The iodine value is expressed as the number of grams of iodine which combine with 100 gm. of the fat or oil.

For example,

0·417 gm. of sperm oil reacted with 25 c.c. of iodine solution ($f = 1·058$ N/10).

$$\text{Iodine value} = \frac{25 \times 1·058 \times 0·0127}{0·417} \times 100 = 80·55.$$

For fuller explanations and practical details, see p. 605 *et seq.*

In addition to the two values mentioned above, other physical and chemical tests are employed in order to identify a fat or oil. The properties involved include specific gravity, refractive index, melting and solidifying points, the acid value, the *Hehner value* and the *Reichert-Meissl value.*

The Hehner value is defined as the percentage of insoluble fatty acids which can be separated from an oil or fat.

The average Hehner value is about 93 to 96.

Butter has a Hehner value from 85 to 88.

The Reichert-Meissl value is defined as the amount of alkali, in cubic centimetres of decinormal potash, required to neutralize the amount of volatile soluble fatty acids liberated and distilled under certain conditions from 5 gm. of fat.

Butter has a Reichert value of about 28, coconut oil of 7·5.

Butter consists of mixed esters of glycerol. The average composition of butter is

	per cent
Fat	83·25
Protein ..	1·0
Lactose ..	0·5
Salts	1·5
Water	13·75

and about 1 to 2 per cent of common salt is added as a preservative.

Butter fat consists of the glycerides of the following fatty acids in the average proportions shown. The first four acids are volatile, the remainder are non-volatile.

				per cent
Butyric acid	..	..	C_3H_7COOH	3·25
Caproic acid	(1·8)	..	$C_5H_{11}COOH$	
Caprylic acid	(0·8)	..	$C_7H_{15}COOH$	4·70
Capric acid	(2·1)	..	$C_9H_{19}COOH$	
Lauric acid	..	..	$C_{11}H_{23}COOH$	4·10
Myristic acid	..	..	$C_{13}H_{27}COOH$	10·3
Palmitic acid	..	..	$C_{15}H_{31}COOH$	28·00
Stearic acid	..	..	$C_{17}H_{35}COOH$	10·00
Arachidic acid	..	..	$C_{19}H_{39}COOH$	0·75
Oleic acid	..	..	$C_{17}H_{33}COOH$	34·75
Linoleic acid	..	..	$C_{17}H_{31}COOH$	4·50

Butter has a density between 0·865 and 0·868 at 100° C.; m. pt. 28 to 34·7° C. It is insoluble in water, soluble in alcohol, and very soluble in ether, chloroform, benzene, petroleum ether, &c.

It is sometimes adulterated with margarine or with coconut fat and coloured with annatto obtained from the fruits of the *Bixa orellana* tree. Other colouring matters employed are juice of carrots, marigolds, saffron, and curcuma.

Food laws demand that butter shall not contain more than 16 per cent of water, and that only common salt shall be used as a preservative (1927).

Margarine may be regarded as an emulsion of animal and vegetable oils with milk, which is stabilized by special chemicals.

There are two classes of margarines:

I. Vegetable margarines, in which vegetable oils predominate.

II. Oleo-margarines, in which animal fats and oils predominate.

These fats and oils, containing glycerides of the same fatty acids as occur in butter, are blended so as to produce a substance having approximately the same chemical composition as the natural product.

The following substances are employed to produce the required result:

(*a*) Vegetable oils: Cotton seed, coconut, palm, arachis (ground nut).

(*b*) Animal fats: lard, premier jus (ox-suet), oleo oil, &c.

These fats and oils are first carefully refined, then churned with pasteurized soured cream or milk, which gives them a buttery flavour as well as acting as an emulsifying agent.

Manufacture.—I. *By the Hydrogenation Process.* In this process the unsaturated portion of oils, such as olein, which is a liquid at ordinary temperatures and contains three unsaturated bonds, is converted into solid saturated stearin by the addition of hydrogen atoms:

$$CH_3(CH_2)_7 \cdot CH{=}CH(CH_2)_7 \cdot COOCH_2$$
$$CH_3(CH_2)_7 \cdot CH{=}CH(CH_2)_7 \cdot COOCH + 3H_2$$
$$CH_3(CH_2)_7 \cdot CH{=}CH(CH_2)_7 \cdot COOCH_2$$
$$\text{Olein}$$

$$CH_3(CH_2)_{16} \cdot COO \cdot CH_2$$
$$= CH_3(CH_2)_{16} \cdot COO \cdot CH$$
$$CH_3(CH_2)_{16} \cdot COO \cdot CH_2$$
$$\text{Stearin}$$
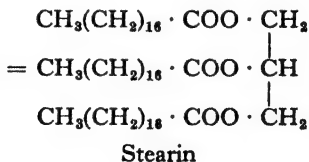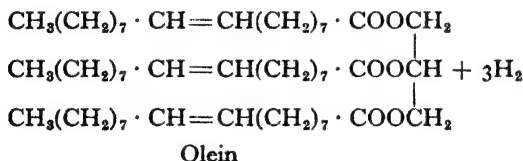
The conversion of olein into stearin, brought about by passing hydrogen through the oil in the presence of nickel powder as a catalyst, is known as **hardening.** The resulting fat is then churned up with cream.

The conversion of an unsaturated acid into a saturated one is conducted in a similar manner:

$$C_{17}H_{33} \; COOH + H_2 = C_{17}H_{35} \; COOH$$

Oleic acid   Stearic acid
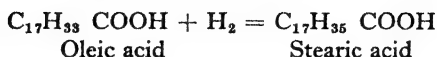
Hydrogenated or hardened fats are also used for soap-making.

II. *By the Sweating Process.*—In this process beef tallow or suet is melted to free it from the membrane and then left to crystallize at 24° C. The fat is next subjected to pressure, in order to separate the solid tristearin from the lower boiling constituents, such as oleo-oil. The liquid which runs off is allowed to cool and a buttery mass is obtained. This mass is mixed with a small quantity of ground nut or sesame oil and finally churned up with milk.

In both cases a margarine cream is obtained which is either discharged down an inclined chute where it is solidified by a stream of ice-cold water, or (preferably) sprayed between .two rotating cylinders fixed close together and cooled internally by brine. The cream solidifies on the cylinders, is scraped off in the form of fine flakes, and allowed to mature in order to obtain a perfect cohesion of the particles or crystals, giving a product similar in appearance to butter.

Classification of Fats and Oils

Fats and oils may be classified:

I. From the point of view of their origin, into

    1. Fatty oils $\begin{cases} (a) \text{ Animal fats and oils,} \\ (b) \text{ Vegetable fats and oils.} \end{cases}$

    2. Essential oils.

    3. Mineral oils.

    4. Waxes.

1. **Fatty oils** are found in the adipose tissue of animals or in oil cells of seeds or other parts of plants, and, as already

mentioned, they are compounds of glycerol with one or more fatty acids.

2. **Essential oils** are volatile substances which occur in different parts of plants. They have a characteristic odour and flavour, e.g. clove oil, aniseed oil, lemon oil.

3. **Mineral oils** do not contain esters of fatty acids. They are obtained from oil wells, coal, shale, &c., and consist mainly of mixtures of various hydrocarbons, which may be separated by fractional distillation into such products as naphtha, kerosene, lubricating oils, and paraffin wax (p. 67). These oils cannot be saponified (contrast fatty oils).

4. **Waxes** bear some resemblances to fatty oils, as they are esters formed by the union of fatty acids with alcohols not belonging to the glycerol series, e.g. beeswax.

The name wax, however, is sometimes given to a true glyceride, e.g. Japan wax, whilst in other waxes no fatty acids or glycerol are present, e.g. paraffin wax.

Though waxes in general contain no glycerol, they have many properties in common with true glycerides (fats): they can be saponified with alkalis, although the saponification is much more difficult and takes longer.

Beeswax, consisting mainly of myricyl palmitate, can be saponified, giving potassium palmitate and myricyl alcohol:

$$C_{15}H_{31}CO \cdot OC_{30}H_{61} + KOH = C_{15}H_{31}COOK + C_{30}H_{61}OH$$

| Beeswax or the wax " myricin " | Potassium palmitate | Myricyl alcohol |
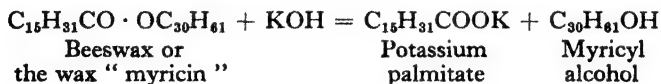
Cerotic acid, $C_{25}H_{51}COOH$, is the other important constituent of beeswax.

Animal and vegetable waxes may be subdivided into:

(a) Liquid waxes, e.g. Sperm oil.

(b) Solid waxes, e.g. Beeswax, Wool grease.

" Lanolin " is purified wool grease; on account of the ease with which it is absorbed by the skin, it forms the basis of many valuable ointments and cosmetics.

II. According to their properties (mineral oils excluded), as follows:

Nature or class	Iodine value
1. Drying oils	Over 140
2. Semi-drying oils	95 to 140
3. Non-drying oils	Under 100
4. Solid fats	1 to 70

1. **Drying oils** consist chemically of glycerine in combination with various fatty acids. They contain unsaturated acids which may possess from one to four double bonds. On exposure to air, these unsaturated acids absorb oxygen and the oil is converted into a hard tenacious skin known as *linoxyn*, the nature of which is unknown; at the same time formaldehyde, carbonic acid, and formic acid are produced. The oxidation of drying oils, therefore, involves complex reactions. The conversion of an oil into an elastic solid is known as the " drying " of the oil, but this term is misleading, for it implies that evaporation of water has taken place, leaving a solid residue, which is not the case.

It is found that the " drying " time of an oil is directly proportional to the amount of unsaturated acids present. Well-known drying oils include linseed oil, tung oil, walnut oil, &c. " Driers " are usually added to drying oils in order to hasten the " drying " or " setting " of an oil, especially in paint manufacture. Driers are compounds which have the property of accelerating the " setting " of linseed oil. A few driers are coloured substances which impart to the paint its characteristic colour. The driers employed in commerce are litharge, red lead, and certain lead and manganese salts such as oleates, rosinates, linoleates, &c.

2. **Semi-drying oils** also absorb oxygen from the air, and become thick, but do not " dry " up completely.

Examples are cotton-seed oil, sesame oil, soya bean oil, mustard oil.

3. **Non-drying oils** do not absorb oxygen from the air, nor do they dry up. Examples are olive oil, arachis oil, castor oil, almond oil.

Marine animal oils, e.g. cod liver oil, whale oil, have an iodine value over 140 but have non-drying properties, and so can be distinguished from drying oils.

4. **Solid fats** have a melting point above 20° C., and a low iodine value. Examples include cacao butter, shea butter.

✓ **Soaps.**—The term *saponification* was originally applied to the manufacture of soap. Hard soap is the sodium salt, soft soap the potassium salt, of the acids of fat. When caustic soda or caustic potash is boiled with a fat, saponification results and a soap is formed. In the case of stearin the reaction is represented as follows:

$$\begin{array}{ll}
C_{17}H_{35}CO\cdot O\cdot CH_2 \quad OH \cdot Na & CH_2OH \\
\qquad\qquad\qquad\quad | & \qquad\qquad\qquad | \\
C_{17}H_{35}CO\cdot O\cdot CH + OH \cdot Na = 3C_{17}H_{35}COONa + CH\cdot OH \\
\qquad\qquad\qquad\quad | & \qquad\qquad\qquad | \\
C_{17}H_{35}CO\cdot O\cdot CH_2 \quad OH \cdot Na & CH_2OH \\
\quad\text{Stearin} & \text{Sodium stearate} \quad \text{Glycerol}
\end{array}$$
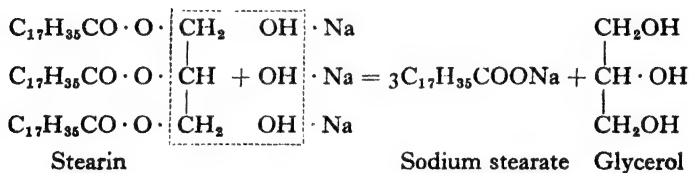
A hard soap therefore consists of the sodium salts of stearic, palmitic and oleic acids. The sodium and potassium soaps are soluble in water. The soaps are " salted out " of their aqueous solutions by the addition of common salt, as they are insoluble in the brine formed. The potassium soaps are converted into the sodium soaps by this " salting out " process:

$$C_{17}H_{33}COOK + NaCl = C_{17}H_{33}COONa + KCl$$
Potassium oleate
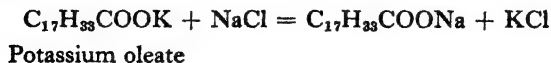
These soaps form a clear solution when dissolved in a little

water, but in a larger quantity of water they are partially hydrolysed:

$$C_{17}H_{35}COONa + HOH \rightleftharpoons C_{17}H_{35}COOH + NaOH$$
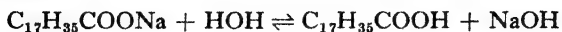
The cleansing action of soap is usually attributed to the presence of the small amount of free alkali formed.

The calcium, barium and magnesium soaps are insoluble in water and hence a precipitate of the calcium soap is formed when " hard " water is used with soap.

The lead soaps are formed by boiling fats with lead oxide and water and were formerly used in medicine under the name of " lead plaster ".

Lead and manganese soaps (made from linseed oil) dissolved in linseed oil and thinned with turpentine or benzene form the liquid " driers " of painters, used to hasten the drying of raw linseed oil (see p. 231).

Floating soaps are sodium soaps, usually made from coconut oil, in which the specific gravity of the soap is lowered by filling the soap with minute air bubbles.

The so-called " liquid soaps " used in lavatories are solutions of potassium coconut oil soaps and glycerol in water. They usually contain from 15 to 20 per cent of anhydrous soap and from 5 to 10 per cent of glycerol. Some contain glucose instead of glycerol. Many of them contain a small amount of free oleic acid.

Calcium soaps, usually called lime soaps, made by the action of slaked lime on fats, are used in large quantities in the manufacture of lubricating greases.

Zinc stearate is used in toilet powders and for preventing grains in rubber powder sticking together.

Polyhydric Alcohols

These alcohols contain two or more hydroxyl groups, each attached to a different carbon atom. They may be subdivided into groups:

1. Dihydric alcohols or glycols (p. 275), $C_nH_{2n}(OH)_2$.

2. Trihydric alcohols, e.g. glycerine (glycerol), $C_3H_5(OH)_3$.

3. Tetra-, penta-, and hexa-hydric alcohols, e.g. erythritol, $C_4H_6(OH)_4$.

The termination OL is reserved for the alcohols.

Glycerine, Glycerol, Propane 1 : 2 : 3 triol,

$$OH \cdot \overset{1}{C}H_2 \cdot \overset{2}{C}H (OH) \overset{3}{C}H_2 \cdot OH$$
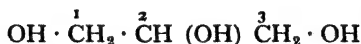
Glycerol is found widely distributed as the alcoholic constituent of fats. It is also found in small quantities in fermented liquors.

Formation.—1. By heating 1 : 2 : 3 trichloropropane with water to 170° C.:

$$\begin{array}{ll} CH_2Cl & CH_2OH \\ | & | \\ CHCl + 3HOH = & CH\ OH + 3HCl \\ | & | \\ CH_2Cl & CH_2OH \end{array}$$
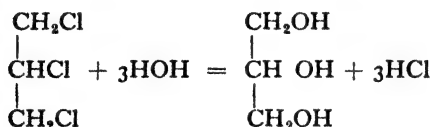
2. From acetylene. Acetaldehyde is produced by absorbing acetylene in sulphuric acid, diluting with water and then distilling:

$$CH\equiv CH + HOH = CH_3CHO$$

The acetaldehyde is then oxidized to acetic acid, from which acetone is prepared: this ketone is converted first into isopropyl alcohol and then into propylene. This olefine unites directly with bromine yielding propylene dibromide, and from the latter, by heating with bromine in presence of iron, glyceryl tribromide, $CH_2Br \cdot CH\ Br \cdot CH_2Br$, is obtained. The three bromine atoms in this compound are next displaced by acetyl groups by digesting with silver acetate, and the product, which is glyceryl acetate, is

hydrolysed with aqueous or alcoholic potash. The complete synthesis of glycerol may be summarized as follows:

$$C_2H_2 \xrightarrow{\text{(H}_2\text{O)}} CH_3CHO \xrightarrow{\text{(O)}} CH_3COOH \longrightarrow (CH_3COO)_2Ca$$

Acetylene   Acetaldehyde   Acetic acid   Calcium acetate

$$\xrightarrow{\text{(Distil)}} CH_3COCH_3 \xrightarrow{\text{(H)}} CH_3CH(OH)CH_3 \xrightarrow{\text{(ZnCl}_2)} CH_3CH{=}CH_2$$

Acetone   Isopropyl alcohol   Propylene

$$\xrightarrow{\text{(Br)}} CH_3CHBrCH_2Br \xrightarrow{\text{(Br)}} CH_2Br \cdot CHBr \cdot CH_2Br$$

Propylene dibromide   Glyceryl tribromide

$$\xrightarrow{\text{(Ag acetate)}} CH_2(CH_3COO)CH(CH_3COO)CH_2(CH_3COO)$$

Glyceryl acetate

$$
\begin{array}{l}
CH_2 \cdot OOC \cdot CH_3 \\
|\\
CH \cdot OOC \cdot CH_3 + 3KOH = \\
|\\
CH_2 \cdot OOC \cdot CH_3
\end{array}
\quad
\begin{array}{l}
CH_2OH \\
|\\
CHOH + 3CH_3COOK \\
|\\
CH_2OH
\end{array}
$$

Glyceryl acetate   Glycerol   Potassium acetate

Alternatively, the propylene may be converted into $C_3H_5Cl_3$ by iodine chloride and treated as in (1) above.

3. *Bio-chemical method*, by fermentation of sugar with yeast, but only 3% of the sugar used is thus converted. This amount may be increased to 38% by bringing about the fermentation of the sugar solution in the presence of large amounts of sodium sulphite. Under these conditions the amount of alcohol formed is diminished and the amount of glycerol is increased:

$$C_6H_{12}O_6 = C_3H_5(OH)_3 + CH_3CHO + CO_2$$

Glucose   Glycerol
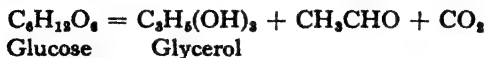
During the World War over a million kilograms of glycerol

per month were made in Germany from beet sugar molasses by this method.

4. By the oxidation of allyl alcohol with dilute potassium permanganate (p. 240):

$$
\begin{array}{ccc}
\text{CH}_2 & & \text{CH}_2\text{OH} \\
\| & & | \\
\text{CH} & + \text{HOH} + \text{O} = & \text{CHOH} \\
| & & | \\
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\
\text{Allyl alcohol} & & \text{Glycerol}
\end{array}
$$
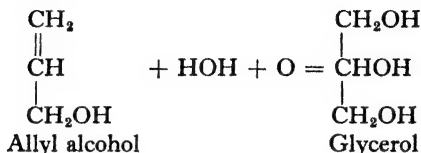
5. *Manufacturing Method.*—The most important source of glycerine is the " spent lyes " of soap manufacture. The lyes are allowed to settle and the soap scum is removed; they are then treated with hydrochloric acid and ferric chloride to precipitate any remaining soap, albuminous substances and fatty acids. The latter are filtered off and the solution is treated with just sufficient alkali to neutralize the acid and to precipitate the iron. The lyes are then concentrated in vacuum evaporators; the salt is deposited in salt boxes and removed at intervals. The recovered salt is used again in the soap works. The evaporation is continued until the lyes contain 80 per cent glycerine. The crude glycerine is then purified by distillation with superheated steam under reduced pressure (50 mm.). Pure glycerine is obtained by redistillation; the distillate when hot is decolorized with animal charcoal and finally filtered.

Another source of commercial glycerine is the fats and oils used in the manufacture of candles. Stearin candles are made from the free acids from fat, separated as far as possible from oleic acid. Several methods are used to hydrolyse the fats into free fatty acids and glycerol:

1. By heating with water under pressure in an autoclave, a small quantity of lime, magnesia, or zinc oxide being added to aid the hydrolysis.

2. By heating with concentrated sulphuric acid to 120° C. This method not only hydrolyses the fats into glycerol and

fatty acids, but also converts the liquid oleic acid into a solid fatty acid:

$$CH_3(CH_2)_7CH = CH(CH_2)_7COOH + HOH$$
$$= CH_3(CH_2)_7CHOH(CH_2)_8COOH$$

Hydroxy-stearic acid
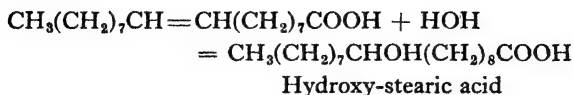
3. By heating with water and Twitchell's reagent. This reagent is made by heating commercial oleic acid and an aromatic hydrocarbon, e.g. naphthalene, with concentrated sulphuric acid and washing out the excess of sulphuric acid with water.

4. By means of a fat-splitting enzyme, *lipase*, found in castor oil seed (*Ricinus communis*).

After the fatty acids have been separated, the glycerine liquor is treated as described above.

Properties.—Glycerine is a colourless, odourless, sweetish syrup, neutral to litmus. It solidifies to a colourless crystalline substance (m. pt. 17° C.) when strongly cooled. It boils at 290° C. under atmospheric pressure. Usually it is distilled under reduced pressure. It is freely soluble in water, alcohols, and acetone, but very sparingly soluble in ether and chloroform. The properties of sweetness and insolubility in ether are frequently found in substances that contain many hydroxyl groups.

Uses.—In medicine as a healing ointment, the dissolved medicament being kept in a moist condition; also as an antiseptic, since it dissolves boric acid, borax, and carbolic acid. Use is made of its hygroscopic properties in the preparation of blacking, self-inking pads, and tobacco (to prevent drying). It is used as a preservative and as a sweetening agent for wines, tinned fruits, and liqueurs. It is added to gas meters and automobile radiators to prevent freezing. Its chief uses are in the manufacture of nitroglycerine and in the textile industry.

Reactions.

1. It reacts with caustic alkalis to form alcoholates. This reaction, however, is reversible:

$$C_3H_5(OH)_3 + 3KOH \rightleftharpoons C_3H_5(OK)_3 + 3HOH$$
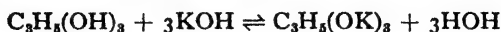
2. As a trihydric alcohol it forms:

A. *Esters*, by the replacement of the hydrogen atoms of the hydroxyl groups by acidic radicles. The hydrogen atoms can be replaced in stages to form glycerol formates, acetates, &c. (known also as mono-, di-, and tri-formin, acetin, &c.).

$$\begin{array}{lll}
CH_2O \cdot CO \cdot CH_3 & CH_2O \cdot CO \cdot CH_3 & CH_2 \cdot O \cdot CO \cdot CH_3 \\
| & | & | \\
CHOH & \rightarrow CH \cdot O \cdot CO \cdot CH_3 \rightarrow & CH \cdot O \cdot CO \cdot CH_3 \\
| & | & | \\
CH_2OH & CH_2OH & CH_2 \cdot O \cdot CO \cdot CH_3 \\
\text{Mono-acetin} & \text{Di-acetin} & \text{Tri-acetin}
\end{array}$$
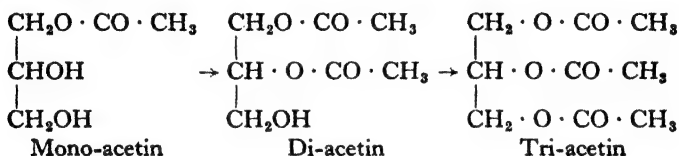
Natural tri-acid esters (glycerides) are found in fats and oils. Glycerol also reacts with inorganic acids such as H_2SO_4, H_3PO_4, HNO_3 and HCl to form esters, e.g. glyceryl sulphuric acid, $C_3H_5(OH)_2O \cdot SO_3H$.

Chlorhydrins (hydrochloric acid esters).

These esters are formed by the action of concentrated hydrochloric acid or of hydrogen chloride on glycerol.

Glyceryl α-monochlorhydrin is formed by heating glycerol with a small quantity of acid at fairly high temperatures or by passing hydrogen chloride into the syrup. One hydroxyl group is replaced by one chlorine atom.

Glyceryl dichlorhydrin is produced when excess of acid is used or when the gas is passed into the glycerine dissolved in acetic acid. Two hydroxyl groups are replaced by two chlorine atoms.

Glyceryl trichloride is obtained by treating the mono- or dichloro-compound with phosphorus pentachloride. It is a colourless liquid (b. pt. 158° C.) which smells like chloroform.

The chlorhydrins are all liquids sparingly soluble in water but readily soluble in alcohol and ether.

$$
\begin{array}{llll}
\alpha\;\; CH_2OH & CH_2Cl & CH_2Cl & CH_2Cl \\
\;\;\;\;\;\;| & | & | & | \\
\beta\;\; CHOH \;\;\to & CHOH \;\;\to & CHOH \;\;\to & CHCl \\
\;\;\;\;\;\;| & | & | & | \\
\alpha'\;\; CH_2OH & CH_2OH & CH_2Cl & CH_2Cl \\
& Glycerol & Glycerol & Glyceryl \\
& \alpha\text{-mono-} & \alpha\alpha'\text{-dichlorhy-} & trichloride \\
& chlorhydrin & drin &
\end{array}
$$
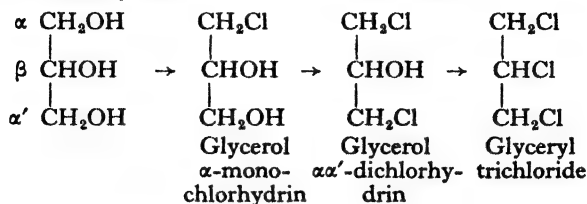
The name *chlorhydrin* does not correctly express their relation to glycerol.

B. *Ethers*, by the replacement of the hydrogen atoms of the hydroxyl groups by alkyl radicles:

$$
\begin{array}{lll}
CH_2O \cdot C_2H_5 & CH_2O \cdot C_2H_5 & CH_2O \cdot C_2H_5 \\
| & | & | \\
CHOH \;\;\;\;\;\;\to & CHOH \;\;\;\;\;\;\to & CHO \cdot C_2H_5 \\
| & | & | \\
CH_2OH & CH_2O \cdot C_2H_5 & CH_2O \cdot C_2H_5 \\
Mono\text{-ethylin} & Di\text{-ethylin} & Tri\text{-ethylin}
\end{array}
$$
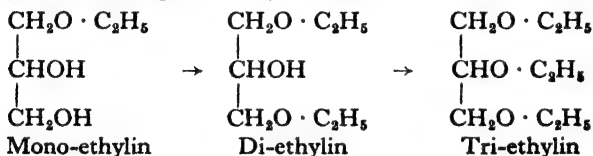
3. It reacts with hydriodic acid or with iodine and phosphorus to form isopropyl iodide. Propylene is formed at the same time:

$$
\begin{array}{llll}
CH_2OH & CH_2I & CH_2 & \\
| & | & \parallel & \\
CH\;OH + 3HI = & CHI + 3HOH \to & CH & + I_2 \\
| & | & | & \\
CH_2OH & CH_2I & CH_2I & \\
& & Allyl\ iodide &
\end{array}
$$

$$
\begin{array}{llll}
CH_2 & CH_2 & CH_2 & CH_3 \\
\parallel & \parallel & \parallel & | \\
CH + HI = & CH + I_2 ; & CH + 2HI = & CHI + I_2 \\
| \;\;\;, & | & | & | \\
CH_2I & CH_3 & CH_2I & CH_3 \\
& Propylene & & Isopropyl\ iodide
\end{array}
$$
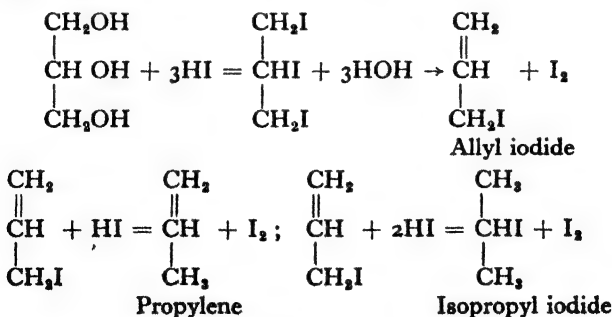
This reaction indicates that glycerol contains a secondary alcoholic group.

4. When distilled with dehydrating agents, e.g. P_2O_5 or

$KHSO_4$, two molecules of water are eliminated and *acrolein* is formed. Acrolein has an acrid and penetrating smell of burnt fat (b. pt. 52° C.).

$$
\begin{array}{ll}
CH_2OH & CH_2 \\
| & \| \\
CHOH - 2HOH = CH \\
| & | \\
CH_2OH & CHO \\
& \text{Acrolein}
\end{array}
$$
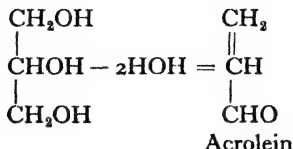
5. It forms esters with nitric acid.

Mononitrin, $C_3H_5(OH)_2(ONO_2)$, and Trinitrin or Nitroglycerine (p. 241), $C_3H_5(ONO_2)_3$, are known.

6. When glycerol is heated with crystallized oxalic acid to 100–110° C., and more oxalic acid crystals are added as soon as the evolution of carbon dioxide ceases, formic acid is produced almost continuously (p. 194).

7. When glycerol is heated with oxalic acid or formic acid to 220° C., the intermediate product glyceryl monoformate (monoformin, p. 194) is decomposed into allyl alcohol and carbon dioxide:

$$
\begin{array}{ll}
CH_2OH & CH_2OH \\
| & | \\
CHOH & \rightarrow CHOH \\
| & | \\
CH_2OH & CH_2O \cdot CO \cdot COOH
\end{array}
$$

$$
\begin{array}{lll}
CH_2OH & CH_2OH \\
| & | \\
\rightarrow CHOH & \rightarrow CH & + CO_2 + H_2O \\
| & \| \\
CH_2O \cdot CHO & CH_2 \\
\text{Monoformin} & \text{Allyl alcohol}
\end{array}
$$
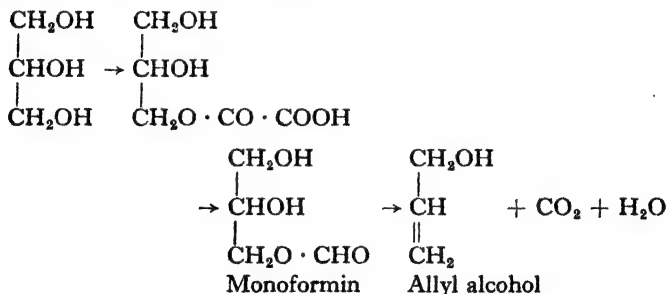
This alcohol is also formed when acrolein is reduced. It is an unsaturated monohydric alcohol and acts both as a primary alcohol and as an olefine. As an alcohol it forms alkyl halides and esters, and when it is cautiously oxidized glycerol is re-formed; further oxidation yields the aldehyde acrolein. As an olefine it forms additive products with

Br_2, HCl, $(CN)_2$ and HClO. Alkyl alcohol is a mobile liquid, sp. gr. 0·871, b. pt. 97° C. It has an irritating odour and is miscible with water.

8. Glycerol yields a variety of oxidation products according to the conditions under which it is treated, since it contains two primary alcohol groups and one secondary.

By the action of dilute nitric acid it is converted into *glyceric* and *tartronic acids*:

$$
\begin{array}{ccc}
CH_2OH & CH_2OH & COOH \\
| & | & | \\
CHOH\,(+\,2O) \rightarrow & CHOH\,(+4O) \rightarrow & CHOH \\
| & | & | \\
CH_2OH & COOH & COOH \\
& \text{Glyceric acid} & \text{Tartronic acid}
\end{array}
$$
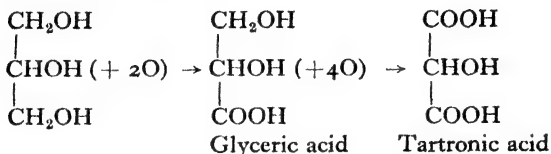
Under other conditions mesoxalic acid, $COOH\,.\,CO\,.\,COOH$, or acids with a smaller number of carbon atoms are obtained, e.g. glycollic acid, $CH_2OH\ COOH$; oxalic acid, $(COOH)_2$, &c.

·9. It yields normal butyl alcohol, caproic acid, and butyric acid by certain fermentations.

10. Only one of the hydrogen atoms is displaced by sodium at the ordinary temperature, i.e. it acts as a monohydric alcohol. The resulting product $C_3H_5(OH)_2\,.\,ONa$ is hygroscopic and is immediately decomposed by water.

The constitution of glycerol follows from its methods of formation and also from its relation to tartronic acid and from its reactions: each of the three hydroxyl groups is attached to a separate carbon atom. It is a trihydric alcohol.

Tests for Glycerol.

1. Heat with potassium hydrogen sulphate: acrolein is formed (intolerable odour and irritating to the eyes).

2. Heat a borax bead with glycerol: boric acid is set free, which colours the flame green.

3. When potassium hydroxide solution is added to copper sulphate solution containing glycerol, no precipitate is formed.

Nitro-glycerine, Glyceryl trinitrate, Nobel's Oil,
$C_3H_5(ONO_2)_3$.

Sobrero (1846) first prepared nitro-glycerine by the action of nitric acid on glycerine. Alfred Nobel (1862), a Swedish engineer, used this compound as a constituent in the manufacture of explosives employed for blasting purposes or as propellants.

Nitro-glycerine is prepared by slowly adding glycerine (1 part) to an ice-cooled mixture of concentrated nitric acid (2 parts) and concentrated sulphuric acid (4 parts). The glycerine, previously warmed to 30° C., is introduced into the acid mixture by means of an injector:

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(ONO_2)_3 + 3H_2O$$

The temperature of the solution is not allowed to rise above 20° C. The sulphuric acid added acts as a dehydrating agent during the reaction. The mixture is allowed to stand, to complete the nitration, and is then carefully poured into ice-cold water, when the nitro-glycerine separates as a heavy oil. The supernatant aqueous solution is decanted off, and the oil transferred to a separating funnel, washed first with water, then with dilute sodium carbonate solution to neutralize any acid present, and finally with much water. The lower layer is run off as completely as possible and freed from any water by filtering it through a mat of sponges.

Properties.—Heavy colourless oil, m. pt. 8° C., sp. gr. 1·6. It has a sweetish taste and is poisonous. It is insoluble in water and alcohol but soluble in ether. It burns without explosion but is a most dangerous substance to handle. When rapidly heated or struck with any metallic instrument it explodes with great violence; moreover, if impure it is liable to explode spontaneously. The explosive decomposition of Nobel's oil yields gases which occupy 10,000 times the volume of the original substance:

$$4C_3H_5(ONO_2)_3 = 12CO_2 + 10H_2O + 6N_2 + O_2$$

This accounts for the enormous explosive power of the substance. It is hydrolysed by alkalis and by $(NH_4)_2S$:

$$C_3H_5(ONO_2)_3 + 3KOH = C_3H_5(OH)_3 + 3KNO_3,$$
$$C_3H_5(ONO_2)_3 + 12(NH_4)_2S = C_3H_5(OH)_3 + 27NH_3 + 6H_2O + 12S.$$

Nitro-glycerine   Glycerol

It is therefore a nitrate and not a nitro-derivative. Hence its name is a misnomer.

Uses.—In the manufacture of dynamite and of blasting gelatine. *Dynamite* is made by adding nitroglycerine (3 parts) to kieselguhr (1 part), and is detonated by fulminate of mercury.

In minute doses nitro-glycerine is used in medicine for cases of heart disease. The pharmaceutical preparations *Tabellæ Trinitrini* and *Liquor Trinitrini* contain nitro-glycerine.

QUESTIONS

1. What is the chemical constitution of a fat? Give the experimental methods for the determination of (*a*) the saponification number, (*b*) the iodine value of a fat. (*Pre. Med.*)

2. What do you understand by each of the following: polymerization, tautomerism, " aldol " condensation, hydrolysis, saponification? Illustrate by reference to examples.

3. What are the chief differences between natural fatty oils and oils derived from petroleum?

Explain, with examples, the terms (*a*) saponification, (*b*) hydrogenation, (*c*) " drying ", of fatty oils.

(*Civil Service: Executive Group.*)

4. What is (*a*) a glyceride, (*b*) a soap, (*c*) a mineral oil, (*d*) an emulsion?

How would you examine an oil in order to ascertain whether it was of vegetable or of mineral origin?

5. Describe the process of manufacture of glycerol. Explain the reactions which prove its constitution, and show how this may be confirmed by synthesis. (*Chemists and Druggists Qual.*)

6. Explain carefully what is meant by the iodine value of a fat? How is this quantity estimated? What other determinations

are carried out with a view to elucidating the nature of fats?
(*Phar. Chem. Qual.*)

7. What products may be obtained by the action of the following acids on glycerol: (*a*) sulphuric; (*b*) hydrochloric; (*c*) nitric; (*d*) oxalic?

State briefly the conditions necessary in each case.

(*Chemists and Druggists Qual.*)

8. What is a soap? Describe the effect of adding a soap solution to (*a*) hard water, (*b*) alum solution, (*c*) dilute hydrochloric acid, (*d*) a saturated solution of common salt.

Write an account of the chemical changes involved in obtaining glycerol from stearin.

9. What products can be obtained by the action of the following substances on glycerol· (*a*) potassium bisulphate, (*b*) sulphuric acid, (*c*) oxalic acid, (*d*) hydrochloric acid, (*e*) nitric acid? Give the necessary conditions in each case.   (*Phar. Chem. Qual.*)

10. Describe and explain the preparation of glycerine from fat.

In winter glycerine, $C_3H_5(OH)_3$, is sometimes added to the water in the radiators of cars to prevent freezing. Calculate the freezing point of a mixture containing 10 per cent by weight of glycerine, assuming that the usual rule is obeyed, whereby a gram-molecular weight of the solute in 100 gm. of water causes the freezing point to fall by 18·6 Centigrade degrees. In practice, a mixture of the concentration mentioned freezes at $-1·6°$ C. Suggest a reason for the discrepancy in your answer.

(*Civil Service: Customs and Excise.*)

11. Explain the meaning of the following terms: condensation, primary amine, optical activity, soap. Give examples.

12. Describe briefly the commercial preparation of glycerol. What reaction takes place between glycerol and (*a*) oxalic acid, (*b*) potassium hydrogen sulphate, (*c*) a mixture of nitric acid and sulphuric acids? Specify the conditions of experiment in each case.   (*B.Sc., London, General.*)

13. How can the constitutional formula of glycerol be established? Define (*a*) saponification number; (*b*) iodine number. Calculate these two constants with reference to a suitable glycerol ester. What use is made of these values in the investigation of a fat?   (*II. M.B., London.*)

Hydroxy Monobasic Acids and their Derivatives

These acids have the general formula:

$$C_nH_{2n}O_3 \quad \text{or} \quad C_nH_{2n} \cdot OH \cdot COOH$$

The following acids will be taken to represent this class:

Glycollic acid or Hydroxy-acetic acid, $CH_2OH \cdot COOH$;
Lactic acid or Hydroxy-propionic acid, $CH_3CHOH \cdot COOH$.

They are mono-hydroxy derivatives of the fatty acids and are named accordingly. They contain both a carboxyl group and an alcoholic (hydroxyl) group, and hence can form derivatives similar to those of monobasic acids and those of alcohols, and also mixed derivatives involving both the acidic group and the alcoholic group.

Glycollic acid and lactic acid, the first two members of the series, are syrupy liquids and can easily be converted into anhydrides. On heating, however, they decompose. Both acids are readily soluble in water and to a lesser extent in alcohol and in ether.

Glycollic Acid, Hydroxy-acetic Acid, $CH_2OH \cdot COOH$.

Occurrence.—In unripe grapes and in the leaves of the wild grape (*Ampelopsis hederacea*), Virginia creeper, &c.

Formation.

1. By oxidizing glycol (p. 275) with dilute nitric acid; some other products, however, are formed at the same time:

$$\begin{array}{ccc} CH_2OH & & CH_2OH \\ | & + 2O = & | & + H_2O \\ CH_2OH & & COOH \\ Glycol & & Glycollic\ acid \end{array}$$
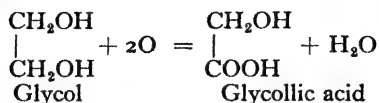
This reaction is important in that a primary alcohol group —CH_2OH is converted into a carboxyl —$COOH$ group.

2. By hydrolysing formaldehyde cyanhydrin with hydrochloric acid:

$$\begin{array}{ccc} CH_2OH & & CH_2OH \\ | & + 2H_2O + HCl = & | & + NH_4Cl \\ CN & & COOH \\ Formaldehyde & & Glycollic \\ cyanhydrin & & acid \end{array}$$
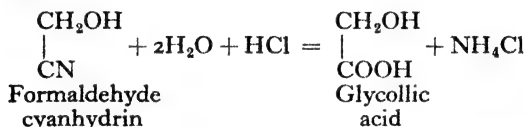
This method is employed in the synthesis of glycollic acid.

3. *Manufacturing process:* by hydrolysing chloracetic acid. *In the laboratory:* by boiling a concentrated aqueous solution of potassium chloracetate, evaporating under reduced pressure and extracting the free acid with acetone:

$$\begin{array}{ccc} CH_2Cl & & CH_2OH \\ | & + HOH = & | & + KCl \\ COOK & & COOH \\ Potassium & & \\ chloracetate & & \end{array}$$
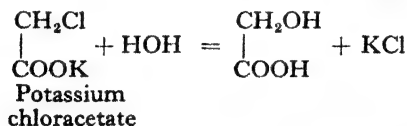
Properties.—Hygroscopic crystalline solid, m. pt. 80° C. Soluble in water, ether, and alcohol. It is a stronger acid than acetic acid.

Reactions 1.—As a **Primary Alcohol.**

Glycollic acid can be oxidized, acetylated, &c., like ethyl alcohol:

$$\begin{array}{ccc} CH_2OH & & CHO \\ | & + O = & | & + H_2O \\ COOH & & COOH \\ & & Glyoxylic\ acid \end{array}$$
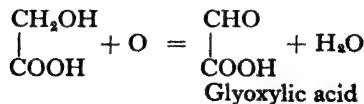
This reaction exemplifies the conversion of a primary alcohol group —CH_2OH into an aldehyde group —CHO. On further oxidation glyoxylic acid is converted into oxalic acid.

$$\begin{array}{l} CHO \\ | \quad\quad + O \\ COOH \end{array} = \begin{array}{l} COOH \\ | \\ COOH \end{array}$$

Glyoxylic acid   Oxalic acid
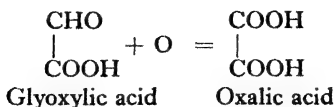
2. As a **Carboxylic Acid.**

Glycollic acid can be neutralized to form salts such as

Sodium glycollate, $CH_2OH \cdot COONa$;

and esterified to form esters such as

Ethyl glycollate, $CH_2OH \cdot COOC_2H_5$.

$$\begin{array}{l} CH_2OH \\ | \quad\quad\quad + HO \cdot C_2H_5 \\ COOH \end{array} = \begin{array}{l} CH_2OH \\ | \quad\quad\quad + H_2O \\ COOC_2H_5 \end{array}$$

Ethyl alcohol   Ethyl
glycollate
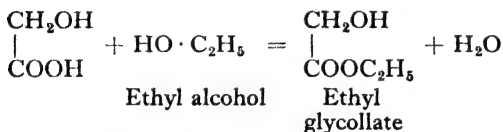
3. As **Alcohol and Acid,** forming mixed derivatives, e.g.

Di-sodium glycollate, $\begin{array}{l} CH_2 \cdot ONa \\ | \\ COONa \end{array}$;

Ethylic ethyl-glycollate, $\begin{array}{l} CH_2 \cdot OC_2H_5 \\ | \\ COO \cdot C_2H_5 \end{array}$.
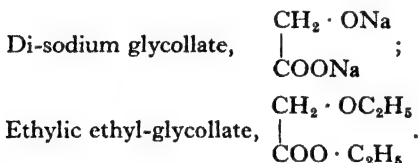
4. When distilled in a vacuum, glycollic acid forms a cyclic or closed chain anhydride, called glycollide, in which the hydroxyl of one molecule has been esterified by the carboxyl of a second molecule:

$$CH_2 \Big\langle{}^{CO \cdot O\,\boxed{H + OH}}_{\boxed{OH + H}\,O \cdot OC} \Big\rangle CH_2 = CH_2 \Big\langle{}^{CO-O}_{O-OC} \Big\rangle CH_2 + 2H_2O$$
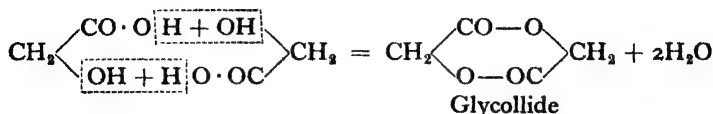
Glycollide

Glycollide is insoluble in cold water (m. pt. 87° C.).

5. Glycollic acid reacts with phosphorus trichloride to form chloro-acetyl chloride, which on hydrolysis gives chloracetic acid:

$$3 \begin{array}{l} CH_2OH \\ | \\ COOH \end{array} + 2PCl_3 = 3 \begin{array}{l} CH_2Cl \\ | \\ COCl \end{array} + 2H_3PO_3;$$

$$\text{Glycollic acid} \qquad \qquad \text{Chloro-acetyl} \\ \text{chloride}$$

$$\begin{array}{l} CH_2Cl \\ | \\ COCl \end{array} + HOH = \begin{array}{l} CH_2Cl \\ | \\ COOH \end{array} + HCl.$$

$$\text{Chloracetic acid}$$

These reactions indicate that glycollic acid has two hydroxyl groups and show the conversion of a chloride group —COCl into a carboxyl —COOH group.

Glycine, Glycocoll, Amino-acetic Acid,
$$CH_2 \cdot NH_2 \cdot COOH.$$

This is the simplest representative of the important class of **amino-acids.**

These acids may be regarded as derived from:

(*a*) The fatty acids, by the replacement of a hydrogen atom of the alkyl radicle by an **amino** (—NH_2) group:

$$CH_3COOH \rightarrow CH_2NH_2COOH$$

(*b*) The amines, by the replacement of one hydrogen atom of the alkyl radicle by a **carboxyl** (—COOH) group:
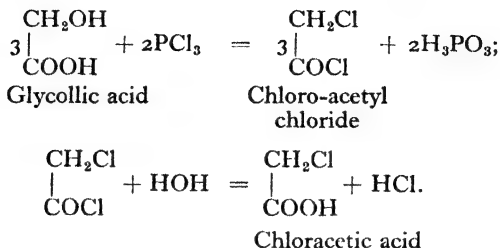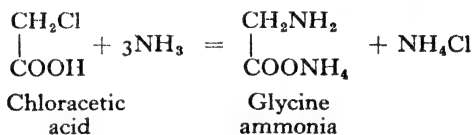
$$CH_3NH_2 \rightarrow CH_2NH_2COOH$$

The amino-acids are both amines and acids, and since the basic amino —NH_2 group counteracts the acidic carboxyl —COOH group these compounds have a *neutral* reaction.

Glycine is of physiological importance and results from the decomposition of such products as the bile, the urine of

horses, uric acid, proteids, and certain albuminoid substances. The name glycocoll is derived from the Greek γλυκύς (*glukus*), sweet, and κόλλα (*kolla*), glue, since it is obtained by boiling glue or gelatine with dilute mineral acids or alkalis and possesses a sweetish taste.

Formation.

1. By chlorinating acetic acid and treating the mono-chloracetic acid with concentrated ammonia:

$$\begin{matrix} CH_2Cl \\ | \\ COOH \end{matrix} + 3NH_3 = \begin{matrix} CH_2NH_2 \\ | \\ COONH_4 \end{matrix} + NH_4Cl$$

Chloracetic	Glycine
acid	ammonia

The glycine ammonia is separated from the ammonium chloride by boiling the solution with copper carbonate or copper hydroxide; copper glycine is formed:

$$2CH_2NH_2 \cdot COONH_4 + CuCO_3$$
$$= (CH_2NH_2 \cdot COO)_2Cu + 2NH_3 + CO_2 + H_2O$$
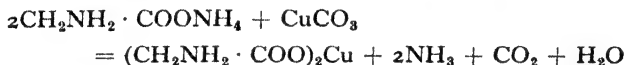
On cooling, the copper glycine separates out in deep blue needles which are filtered off, dissolved in hot water and decomposed with hydrogen sulphide. The precipitated copper sulphide is separated by filtration and the filtrate is concentrated until the glycine begins to crystallize.

2. By boiling glue* or gelatine with alkalis, e.g. baryta water, and treating the resulting compound with dilute sulphuric acid:

$$\begin{array}{ccc} [Ba(OH)_2] & & [H_2SO_4] \\ (C_6H_{10}N_2S)_n \longrightarrow (C_2H_4NO_2)_2Ba \longrightarrow CH_2NH_2 \cdot COOH \end{array}$$

Glue	Glycine

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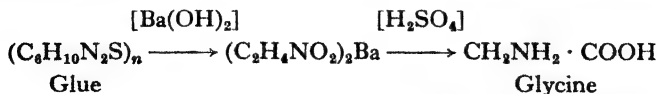
* The formula given for glue represents the average composition although the sulphur content varies in different specimens.

3. By decomposing hippuric acid, i.e. benzoyl glycine, with concentrated hydrochloric acid:

$C_6H_5CO \cdot NH \cdot CH_2 \cdot COOH + H_2O + HCl$
Hippuric acid

$$= C_6H_5 \cdot COOH + CH_2NH_2COOH \cdot HCl$$

or, structurally,

$CO \cdot NH \cdot CH_2 \cdot COOH$ COOH

$+ H_2O + HCl \;\; =$ $+ \begin{matrix} CH_2 \cdot NH_2 \cdot HCl \\ | \\ COOH \end{matrix}$

Hippuric acid   Benzoic   Glycine
(Benzoyl glycine)   acid   hydrochloride
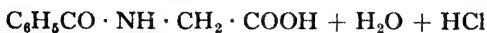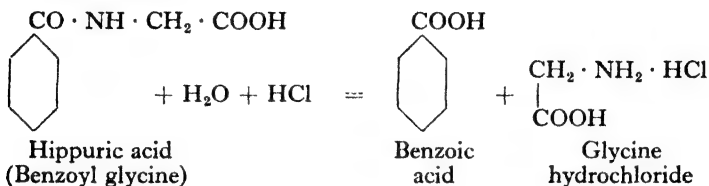
This reaction shows that glycine has basic properties.

Properties.—Colourless rhombic crystals, m. pt. 235° C. It has a sweet taste; it is readily soluble in water and its aqueous solution gives a deep red coloration with ferric chloride. It is insoluble in absolute alcohol and in ether. Its acid properties are indicated by the formation of an ethyl ester, an amide, &c. When heated with barium monoxide or soda-lime, it is decomposed into methylamine and carbon dioxide:

$$CH_2 \cdot NH_2 \cdot COOH = CH_3NH_2 + CO_2$$
Glycine   Methylamine

It differs from an amide in that it does not evolve ammonia when heated with a solution of sodium hydroxide, but forms a salt, sodium amino-acetate:

$$\begin{matrix} CH_2 \cdot NH_2 \\ | \\ COOH \end{matrix} + NaOH = \begin{matrix} CH_2 \cdot NH_2 \\ | \\ COONa \end{matrix} + H_2O$$
Sodium amino-acetate
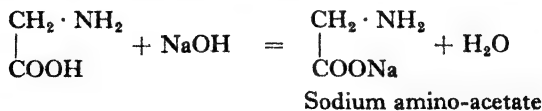
With nitrous acid it reacts like a primary amine, the amino

group being displaced by a hydroxyl group, with the formation of glycollic acid:

$$CH_2 \cdot | N | H_2 | \cdot COOH \qquad CH_2OH$$
$$+ OH | N | O | \qquad = \qquad | \qquad + N_2 + H_2O$$
$$COOH$$

It reacts with strong acids to form salts:

$$CH_2 \diagup^{NH_2 \cdot HCl}_{\diagdown COOH} \; ; \qquad CH_2 \diagup^{NH_2 \cdot HNO_3}_{\diagdown COOH}$$

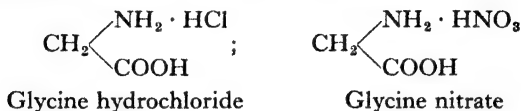Glycine hydrochloride   Glycine nitrate

It reacts with formaldehyde to form methylene aminoacetic acid. This acid may be estimated by titration with a standard solution of sodium hydroxide, using phenolphthalein as an indicator (see p. 616):

$$CH_2 \cdot NH_2 \qquad\qquad CH_2 = N = CH_2$$
$$| \qquad + H \cdot CHO \quad = \qquad | \qquad + H_2O$$
$$COOH \qquad\qquad COOH$$

Formaldehyde   Methylene amino-acetic acid
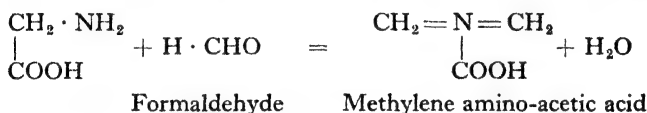
It forms alkyl and acyl derivatives such as:

A. **Sarcosine, Methyl glycine,** $CH_2 \cdot NH(CH_3)COOH$, in which a methyl group replaces a hydrogen atom of the amino group in the parent substance.

Formation.

1. By the action of methylamine on either chloracetic acid or glycine:

$$CH_3 \cdot NH \cdot \boxed{H + Cl} \cdot CH_2 \qquad CH_3 \cdot NH \cdot CH_2$$
$$| \qquad\qquad = \qquad\qquad | \qquad + HCl$$
$$COOH \qquad\qquad\qquad COOH$$

Methylamine   Chloracetic acid   Sarcosine

$$CH_3 \cdot NH \cdot \boxed{H + NH_2} \cdot CH_2 \cdot COOH = CH_3 \cdot NH \cdot CH_2COOH + NH_3$$

Glycine   Sarcosine
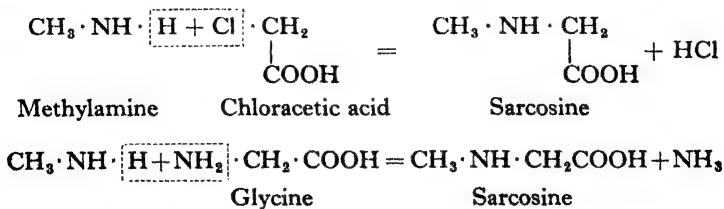
2. By the decomposition of the complex natural substances **creatine** $(NH_2)(NH)C \cdot N(CH_3)CH_2 \cdot COOH$, a constituent of muscle and found in meat broth, and **caffeine,** $C_8H_{10}N_4O_2$, found in both tea and coffee:

$$\begin{array}{c} H_2N \\ \diagdown \\ HN \diagup \end{array} C \begin{array}{|c} \ \\ \ \end{array} NCH_3CH_2COOH$$
$$+ \qquad \text{Creatine}$$
$$HO \begin{array}{|c} \ \end{array} H$$

$$= \begin{array}{c} NH_2 \\ \diagdown \\ NH_2 \diagup \end{array} CO + CH_3 \cdot NH \cdot CH_2COOH$$
$$\text{Urea} \qquad\qquad \text{Sarcosine}$$
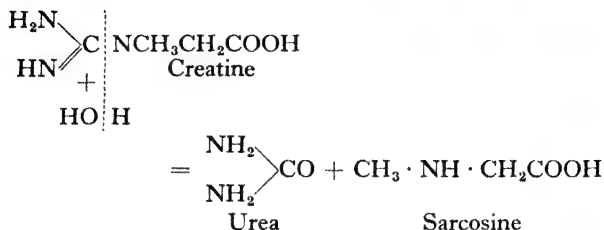
B. **Betaine, Trimethyl glycine,** is formed by the action of trimethylamine on chloracetic acid:

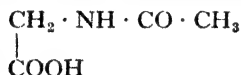$$\begin{array}{l} CH_2 \cdot Cl \\ | \qquad\qquad + N(CH_3)_3 = \\ COOH \end{array} \begin{array}{l} CH_2 \cdot N(CH_3)_3 \begin{array}{|c} Cl \end{array} \\ | \\ COO \begin{array}{|c} H \end{array} \end{array} = \begin{array}{l} CH_2 - N(CH_3)_3 \\ | \qquad\quad | \quad + HCl \\ CO - O \end{array}$$

Chloracetic   Trimethyl-   Betaine   Betaine
acid   amine   hydrochloride
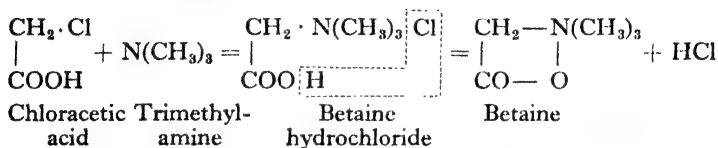
Betaine is found in many plants and occurs in considerable quantity in beetroot and hence in beet sugar molasses.

C. **Aceturic Acid, Acetyl glycine,**

$$\begin{array}{l} CH_2 \cdot NH \cdot CO \cdot CH_3 \\ | \\ COOH \end{array}$$

D. **Dimethyl glycine** is formed by the action of dimethylamine on chloracetic acid:

$$\begin{array}{l} CH_2 \begin{array}{|c} Cl \end{array} \\ | \qquad + \begin{array}{|c} H \end{array} N(CH_3)_2 = \\ COOH \end{array} \begin{array}{l} CH_2 \cdot N(CH_3)_2 \\ | \qquad\qquad\quad + HCl \\ COOH \end{array}$$

Chloracetic   Dimethylamine   Dimethyl glycine
acid
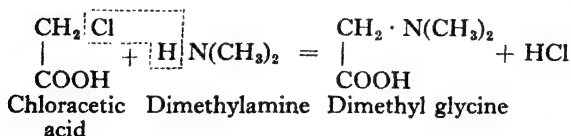
All these derivatives may be regarded as substituted amino-acids.

Note.—An **acyl** or acid organic radicle is the monovalent radicle left when —OH is removed from the molecule of each acid. These radicles end in YL, e.g.:

> Acetyl,　　CH_3CO—
> 　　　from Acetic acid, $CH_3 \cdot COOH$;
>
> Propionyl, CH_3CH_2CO—
> 　　　from Propionic acid, $CH_3 \cdot CH_2 \cdot COOH$;
>
> Butyryl,　　$CH_3CH_2CH_2CO$—
> 　　　from Butyric acid, $CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$.

It seems probable that amino-acetic acid and other amino-acids are inner ammonium salts or intramolecular salts formed by the union of the carboxyl acid group with the NH_2 basic constituent. The absence of a free —COOH group in many amino-acids is indicated by the fact that many of them are not acted on by diazo-methane, CH_2N_2, a very reactive compound which with acids forms methyl esters. According to this view, the structure of glycine may be represented by a closed-chain formula:

$$
\begin{array}{l}
NH_3\!\!-\!\!-\!\!-\!\!-\!\!-\!\! \\
| \qquad\qquad\ \ \rangle O \\
CH_2\!\!-\!\!CO
\end{array}
$$
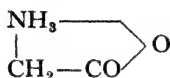
Isomerism of the Hydroxy-Acids

Monohydroxy-acids can be formed from fatty acids by substituting one hydroxyl group for a hydrogen atom attached to a carbon atom other than that of the carboxyl group. Glycollic acid can be formed from acetic acid in this way:

$$CH_3 \cdot COOH \rightarrow CH_2OH\ COOH$$
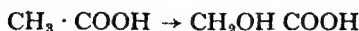
In the case of fatty acids containing more than two carbon atoms, the substitution of an —OH group for a hydrogen atom may take place in two ways, giving isomeric compounds.

The isomerides containing three carbon atoms are related to propionic acid in the manner shown in the following formulæ:

$$CH_3 \cdot CH_2 \cdot COOH$$
Propionic acid

$$\overset{\beta}{CH_3} \cdot \overset{\alpha}{CH(OH)} \cdot COOH \rightarrow (C_3H_6O_3) \leftarrow \overset{\beta}{CH_2} \cdot (OH) \cdot \overset{\alpha}{CH_2} \cdot COOH$$
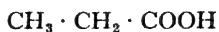
α-hydroxy-propionic acid, β-hydroxy-propionic acid,
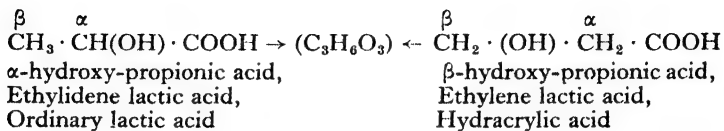Ethylidene lactic acid,   Ethylene lactic acid,
Ordinary lactic acid   Hydracrylic acid

In order to distinguish between these isomerides, the carbon atom next to the carboxyl group is denoted by the Greek letter a, the remaining carbon atoms being denoted by β, γ, &c., as shown. For instance, the compound $CH_2(OH) \cdot CH_2 \cdot CH_2 \cdot COOH$ is known as γ-hydroxy-butyric acid.

It should be noted that there are four acids represented by the formula $C_3H_6O_3$ (see below).

Theory of Space Isomerism (Stereo-isomerism)

Lactic acid (a-hydroxy-propionic acid) has the formula $CH_3 \cdot CH(OH) \cdot COOH$ and contains one carbon atom which is attached to four different groups or monovalent radicles:

$$
\begin{array}{c}
CH_3 \\
| \\
H-\mathbf{C}-OH \\
| \\
COOH
\end{array}
$$
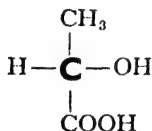
The four valencies of the carbon atom are directed towards the four corners of a regular tetrahedron.

Louis Pasteur (1822–95) was aware that certain solutions exhibit rotatory power, which he attributed to molecular dissymmetry. Following these investigations, Le Bel and van't Hoff (1874) independently put forward the theory of stereo-isomerism. The central carbon atom

to which four different groups are attached is named an **asymmetric carbon atom.**

A compound which contains a single asymmetric carbon atom to which four different radicles are attached can exist in three-dimensional space in two distinct forms, one of which is the mirror image of the other (like the hands or feet).

Fig. 27 (p. 256) shows the two structures for lactic acid, active amyl alcohol, and malic acid. The asymmetric carbon atom is indicated by heavy type.

The two forms cannot exist in two dimensions, for in that case the mirror image can be superposed on the object.

A clearer conception of this type of isomerism, which is known as **stereo-isomerism,** may be obtained by using atomic models. The carbon atom is represented by a large black ball and its atom-forming power by four sockets. Other atoms or groups of atoms are represented by differently coloured balls. Four differently coloured balls (representing four different groups) are fixed to the four sockets to represent the object, and two are interchanged in another model to represent the image. It will be found impossible to place these models so that the coloured balls occupy corresponding positions unless two of the balls in one model are interchanged.

Stereo-isomerism may be defined as a special type of isomerism in which the compound contains an asymmetric carbon atom (i.e. a carbon atom attached to four different monovalent radicles) and is capable of existing in two forms, one form being the mirror image of the other; these forms are known as stereo-isomers.

Stereo-isomers can only be distinguished by their action on polarized light; one form, which rotates the plane of
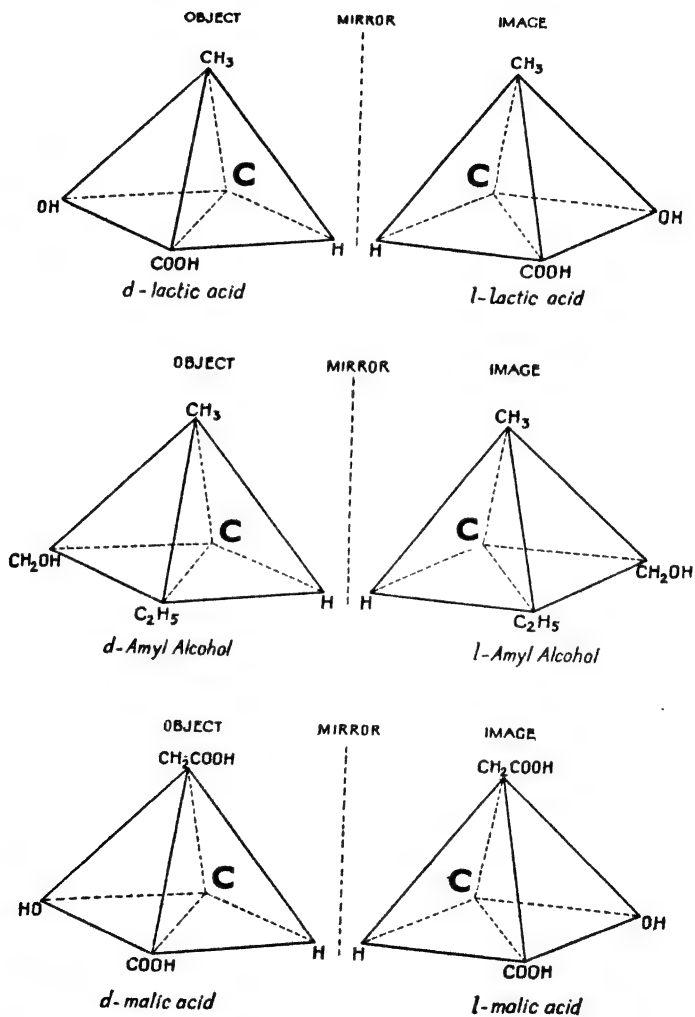
Fig. 27.—Absolute configurations of Lactic Acids, Amyl Alcohols and
Malic Acids

polarization to the right, or clockwise, is known as the **dextro-rotatory** form, and the other, which rotates the plane to the left, or counter-clockwise, is known as the **lævo-rotatory** form.

Optical Rotation or Rotatory Power: The Polarimeter

Many organic liquids and the solutions of many organic solids possess the power of rotating a ray of plane-polarized light. Polarized light is light which has been passed through a Nicol prism, which consists of crystals of Iceland spar cut

Fig. 28.—Laurent's Polarimeter

along their axes and cemented together again in a certain position with Canada balsam. The effect of a Nicol prism is such that the emergent beam of light consists of rays which are all vibrating in the same plane.

The instrument used to measure the degree of rotation is known as a polarimeter. Laurent's polarimeter is shown in fig. 28.

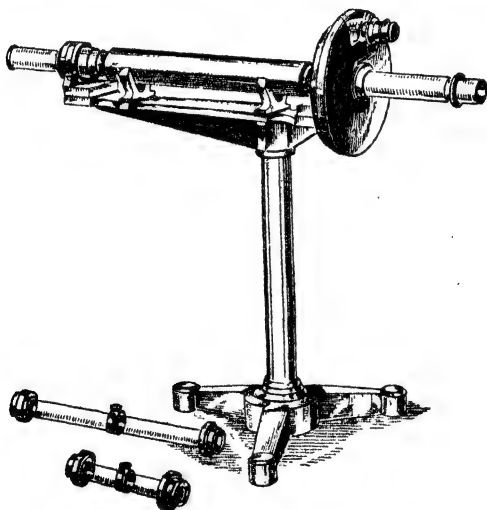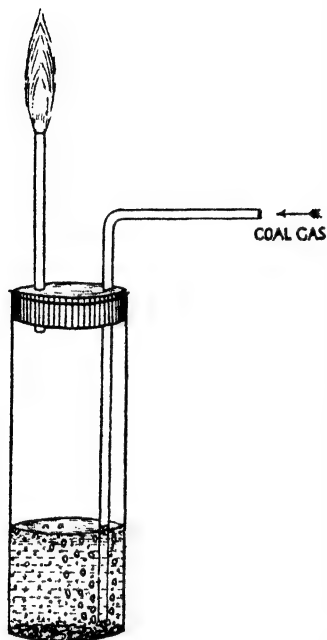The rotation varies with the wave-length of the light used. Hence monochromatic light must be used in determinations of optical rotation, and the yellow light, known as sodium D light, produced by the introduction of sodium chloride into a bunsen flame is commonly employed, although the more volatile sodium bromide gives a brighter flame. The green light of the mercury vapour lamp may also be used. In recording results the kind of light used must be stated.

Note.—A sodium flame may be conveniently obtained in the laboratory by introducing into a bottle some granulated zinc and sodium chloride (fig. 29). Dilute sulphuric acid is added to this mixture; the nascent hydrogen liberated forms sodium hydride, which burns in coal gas. The bottle is fitted with a cork containing an inlet tube for coal gas which reaches almost to the bottom of the bottle, and also with a small exit tube made of brass or other metal. When coal gas is passed through the solution the sodium compound is driven over and burns with a bright yellow flame at the mouth of the exit tube. Care must be taken that the air is completely expelled from the bottle by the coal gas. This is done by collecting a sample of gas in a test tube over water, and igniting it. If there is no sign of explosion, the gas may safely be lit at the mouth of the exit tube.

COAL GAS

Fig. 29.—Apparatus for producing a Sodium Flame in the Laboratory

The Polarimeter: Practical Details

Fig. 30 is a diagrammatic sketch of the optical parts of a polarimeter. Monochromatic light from a sodium burner A passes through B, which consists of either a cell containing a solution of potassium dichromate, or a thin plate of this substance. This absorbs the blue or violet rays and so renders the sodium D light purer. The " purified light " then passes through a collimating arrangement of lenses C, which
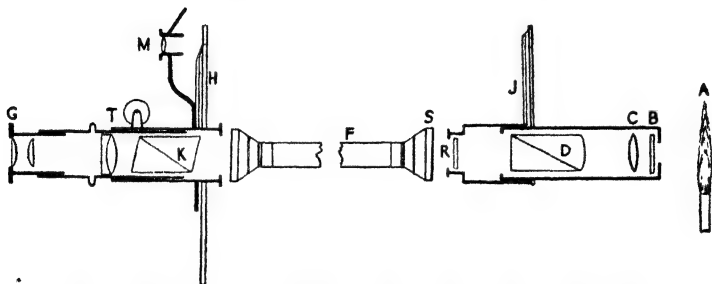
Fig. 30.—Diagrammatic arrangement of the Optical parts of a Polarimeter

concentrates light on the Nicol prism D. The position of the latter can be altered by moving J.

This Nicol prism is known as the *Polarizer*.

The rays of light passing through the polarizer continue through the opening R, where a quartz plate cut parallel to the optic axis is interposed so as to obscure half the field. This plate causes the transmitted light to vibrate in a plane inclined at a definite angle to that of the entering light, and is of such a thickness that it produces a difference of half a wave-length or an odd number of half wavelengths between the two rays which arise by double refraction. The light then passes through the polarimeter tube F of known internal length. This tube contains a column of liquid to be examined. The liquid is admitted into the tube by unscrewing the cap S at one end. Care must be taken to exclude all air bubbles.

The light continues on its way through a second Nicol

prism K, known as the *Analyser*, which is observed by the Galilean telescope GT. The analyser can be rotated by means of a screw independently of the graduated circular disc H. A rack-and-pinion arrangement enables the analyser and telescope to be rotated simultaneously. Attached to the disc are verniers which can be read by means of a movable microscope M.

The student should study the details of a polarimeter and note that rays passing through the polarizer say in a vertical plane are totally extinguished by the analyser when the latter is turned so that rays can only traverse it in a horizontal plane. If the analyser is now rotated, more and more light is transmitted until the planes of transmission coincide, when the field is fully illuminated. The zero point is that point indicated on the scale at which the illumination on both sides of the plate R is equal. This zero point must be accurately found and recorded before every experiment. In a well-adjusted instrument this point should be within a few minutes of the zero of the scale.

The Polarimeter: Theoretical Details.

(*a*) *Light Passage.*—A ray of ordinary light consists of vibrations in all directions in a plane at right angles to the direction of the ray. The transmission of this ray through a polarimeter may be simply explained by comparing it with a string fixed at one end to an upright and made to vibrate in all directions at the other (fig. 31). If this string is passed through a vertical slit (cf. the polarizer) only vertical vibrations are transmitted and if a horizontal slit (cf. the analyser) is introduced subsequently, all the vibrations are eliminated and the string is without movement. When the horizontal slit is turned into a vertical position the vertical vibrations are transmitted (cf. the zero point).

Now a ray of light after passing through the polarizer, when viewed through the telescope, has a plane of vibration which passes unchanged in the half of the field to the

right, uncovered by the quartz plate R. This ray is known as the incident ray (CO in fig. 32 (*a*), p. 262).

When the plane-polarized light falls on the plate it is resolved into two sets of waves travelling along the same path but polarized in planes perpendicular to one another, which are represented by OA and OB respectively. These traverse the quartz at different velocities, and since the quartz is a half-wave plate, i.e. retards one ray by half a wave-

VERTICAL SLIT   VERTICAL SLIT

HORIZONTAL SLIT   VERTICAL SLIT
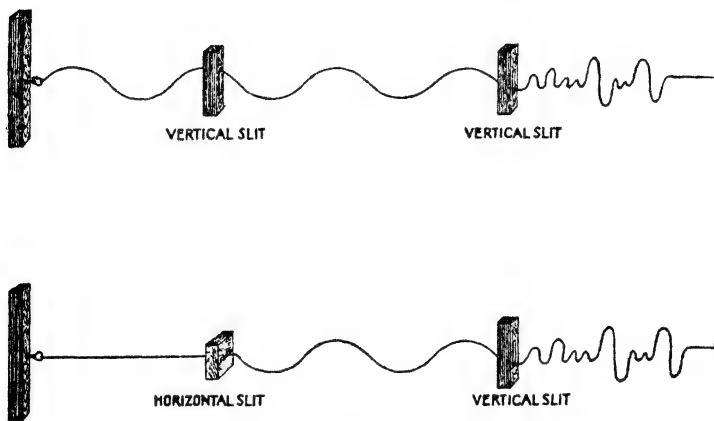
Fig. 31.—To Illustrate the Principles of Polarized Light

length, the emerging rays can be represented by OA and OD (not OB). On emerging, these two combine into a ray polarized in the direction OE such that ∠AOC = ∠AOE, and the angle EOC represents the angle between the directions of the polarized light through the two halves at R.

The polarimeter tube containing pure water or other non-rotating liquid, e.g. ether, is placed in position, and if the analyser is placed parallel to the polarizer, the light in the right half of the field will pass through unchanged, but only a portion of the light which passes through the quartz plate will pass through the analyser; this is represented by OE. If ∠AOC = 45°, then ∠EOC = 90°, and the light in the left half of the field will be extinguished (fig. 32 (*b*)). The

smaller the angle AOC, that is, the smaller the angle between the plane of vibration of the polarized light and the optic axis of the quartz, the greater is the degree of sensitiveness, although the total intensity of illumination is less.

Similarly, if the plane of the analyser is made parallel to OE, there will be a maximum illumination in the left half
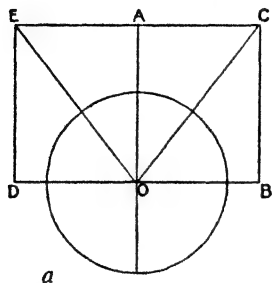
Fig. 32.—To Illustrate the Theory of Illumination of a Polarimeter
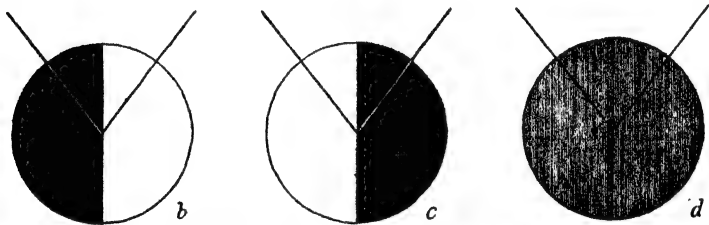
of the field provided that the angle EOC = 90° (fig. 32 (c)). Between these two positions of the analyser there must be a point, known as the zero point, where uniform illumination is observed (fig. 32 (d)), but this illumination will not be bright.

When a polarimeter tube containing an optically active substance is placed in position, the rays OC and OE are rotated through equal angles, and to re-establish uniform illumination the analyser must be turned through an angle equal to the angle of rotation. This rotation is measured on the graduated circular disc. When the analyser is rotated to the right to attain the position of darkness (or to the left

for illumination) the substance is dextro-rotatory: if to the left, the substance is lævo-rotatory.

For further experimental details, see Chap. XXVII, p. 601.

(*b*) *Experimental Results for Homogeneous Liquids.*—It must be noted that the angle of rotation of an optically active substance depends on four main factors:

1. The wave-length of the light used.

2. The nature of the solute and solvent, and the concentration of the solution.

3. The temperature of the solution.

4. The length of the polarimeter tube containing the substance through which the light passes.

These factors are partly included in the following definition:

The Specific Rotation or Rotatory Power of a substance is defined as the angle of rotation produced by 1 gm. of the active substance in 1 c.c. by a layer 1 dm. in length.

This for sodium light (the D line) and temperature t is denoted by

$$\left[\alpha\right]_{D}^{t}.$$

If A is the observed rotation produced for sodium light at a temperature t by a layer of liquid L dm. long, and the density of the liquid is d, then

$$\left[\alpha\right]_{D}^{t} = \frac{A}{d \times L};$$

but if instead of the density the concentration C is known, then

$$\left[\alpha\right]_{D}^{t} = \frac{100 \times A}{C \times L}$$

where C is the number of gm. of the substance in 100 c.c. of solution.

The **Molecular Rotation** is used to compare different optically active substances and consists of the above quantity multiplied by the molecular weight (M) of the compound and divided by 100 in order to avoid unwieldy numbers. It is denoted by

$$\left[M\right]_D^t, \text{ and } \left[M\right]_D^t = \frac{\left[\alpha\right]_D^t \times M}{100}.$$

This is the angle of rotation produced by a layer of active substance 1 mm. thick and containing 1 gm.-molecule in 1 c.c.

Racemic Compounds.

All optically active compounds without exception contain at least one asymmetric carbon atom, but the reverse is not true, for there are compounds containing a carbon atom united by its four bonds to four different elements or groups of atoms which are optically inactive. These compounds are known as **Racemic Compounds.**

Optically active compounds include active amyl alcohol, $C_2H_5 \cdot CH_3CH \cdot CH_2OH$, sarcolactic acid (active lactic acid, p. 269), &c.

Ordinary lactic acid obtained from sour milk, however, is optically inactive, although it contains an asymmetric carbon atom. It is assumed that such a compound is a mixture of dextro- and lævo-lactic acids. Since these stereoisomers turn the plane of polarization through equal amounts to the right and the left respectively, they neutralize one another and form the optically inactive compound. This inactive compound containing an asymmetric carbon atom is known as Inactive (*dl*) or Racemic (*r*) lactic acid.

This assumption that Racemic lactic acid is a combination of equal quantities of the dextro- and lævo-acids is substantiated by the fact that ordinary lactic acid has been resolved

into its two active constituents dextro-lactic acid (sarcolactic acid) and lævo-lactic acid by the fractional crystallization of its strychnine salts.

Lactic Acid, *dl* **- Ethylidene lactic acid,**
$CH_3CH(OH)COOH.$

Occurrence.—In sour milk, in opium, in sauerkraut, and in the gastric juice. Scheele (1780) first isolated ordinary lactic acid from sour milk. Its name is derived from Latin *lac*, milk.

Formation.—1. By the lactic fermentation of sugars, gums and starches by the enzyme *lactase*:

$$
\begin{array}{ccc}
CH_2OH & & COOH \\
| & & | \\
(CHOH)_4 & \longrightarrow & 2\ CHOH \\
| & & | \\
CHO & & CH_3 \\
\text{Glucose} & & \text{Lactic acid}
\end{array}
$$

$$C_{12}H_{22}O_{11} + H_2O = 4C_3H_6O_3$$
Lactose   Lactic acid
(milk sugar)
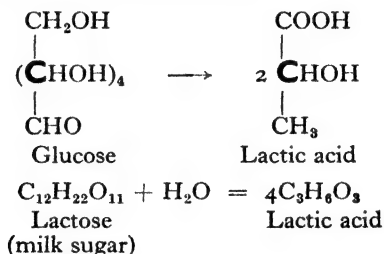
The fermentation is carried out by the action of the micro-organism known as *Bacillus acidi lactici* on an aqueous solution of the sugar or other allied substance at a temperature of 45° C. The free acid is not allowed to accumulate, otherwise it destroys the micro-organism; it is therefore converted into calcium lactate by the addition of chalk, and the free acid is then regenerated by decomposing the calcium salt with sulphuric acid, filtering off the calcium sulphate and concentrating the lactic acid filtrate by evaporation.

This lactic acid fermentation occurs in many practical processes—butter and cheese making, in the making of sauerkraut from cabbage and dill pickles from cucumber, and in the preparation of silage, a cattle food, from fodder.

2. By heating grape or cane sugar with potassium hydroxide solution. From 50 to 60 per cent of the sugar can be converted in this way into the inactive acid.

The relation of lactic acid to the sugars appears at a first glance to be very simple; e.g. grape sugar is a polymer of lactic acid.

3. By the oxidation of $\alpha\beta$-propylene glycol with nitric acid:

$$\begin{matrix} CH_3CH \cdot OH \\ | \\ CH_2OH \end{matrix} + 2O = \begin{matrix} CH_3 \cdot CH \cdot OH \\ | \\ COOH \end{matrix} + H_2O$$

$\alpha\beta$-propylene glycol   Lactic acid
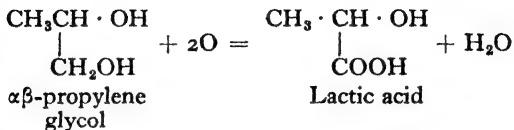
4. By heating α-chloro- or α-bromo-propionic acid with water, dilute aqueous alkalis or silver hydroxide; hydrolysis takes place:

$$\overset{\beta}{CH_3} \cdot \overset{\alpha}{CH} \cdot Br \cdot COOH + H_2O = CH_3 \cdot CH(OH) \cdot COOH + HBr$$

α-bromo-propionic acid
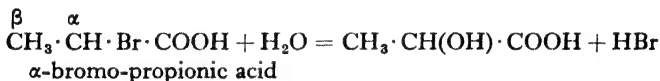
5. By treating α-amino-propionic acid with nitrous acid:

$$\begin{matrix} CH_3 \cdot CH \cdot |N| \cdot H_2 \cdot COOH \\ |+| \\ OH \cdot |N| \cdot O \end{matrix} = CH_3 \cdot CH \cdot OH \cdot COOH + N_2 + H_2O$$
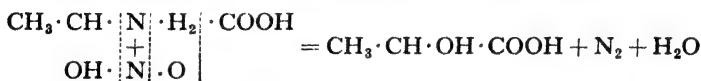
6. Synthetic method, by hydrolysis of acetaldehyde cyanhydrin (p. 171):

$$CH_3 - C\overset{\displaystyle H}{\underset{\displaystyle O}{\big\langle}} \xrightarrow{(HCN)} CH_3 - C\overset{\displaystyle OH}{\underset{\displaystyle CN}{\big\langle H}} \longrightarrow$$

Acetaldehyde   Acetaldehyde cyanhydrin

$$\xrightarrow{(HOH)} CH_3 - CH\overset{\displaystyle OH}{\underset{\displaystyle COONH_4}{\big\langle}} \xrightarrow{(H_2SO_4)} CH_3 - CH\overset{\displaystyle OH}{\underset{\displaystyle COOH}{\big\langle}}$$

Ammonium lactate   Lactic acid
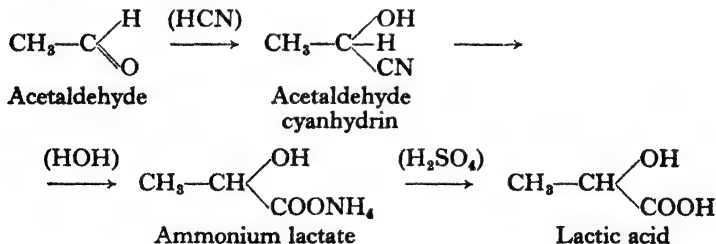
Properties.—Lactic acid is a syrupy, sour, hygroscopic liquid, miscible with water, alcohol and ether in all proportions. It cannot be distilled, as it undergoes decomposition into lactide, aldehyde, water, carbon monoxide, and other

products. To obtain the pure acid it is necessary to distil the crude product under reduced pressure; a crystalline solid melting at 18° C. is obtained.

Reactions.—1. When heated directly it is partially converted into the anhydride, lactide, $C_6H_8O_4$, which is a double ester, and partially into aldehyde, carbon monoxide, and water. Two molecules at first condense with elimination of water. The reaction takes place in stages:

$$CH_3 \cdot CH \diagup^{COOH}_{O\,[H + HO]\, \cdot\, CO} \diagdown^{HO}_{} CH \cdot CH_3$$

$$= CH_3 \cdot CH \diagup^{COOH}_{O} \diagup^{HO}_{CO} CH \cdot CH_3 + H_2O;$$

Lactyl-lactic acid

$$CH_3 \cdot CH \diagup^{CO\,[OH + H]\,O}_{O} \diagup^{}_{CO} CH \cdot CH_3$$

$$= CH_3 \cdot CH \diagup^{CO—O}_{O—CO} CH \cdot CH_3 + H_2O.$$
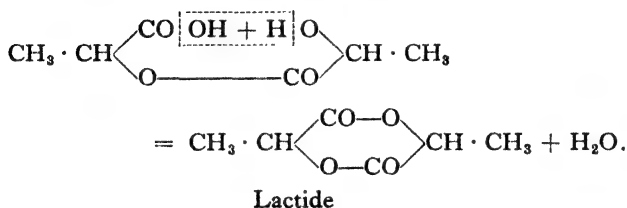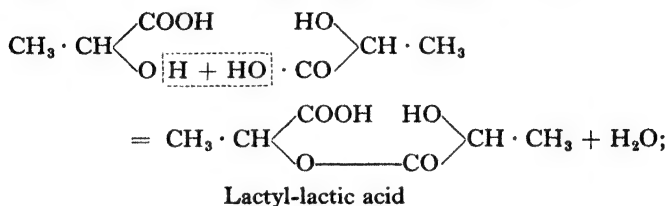
Lactide

This reaction is characteristic of α-hydroxy-acids. Another molecule decomposes as follows:

$$CH_3 \cdot CH \cdot OH \cdot COOH = CH_3 \cdot CHO + CO + H_2O$$

The complete reaction is

$$3C_3H_6O_3 = C_6H_8O_4 + CH_3CHO + CO + 3H_2O$$

| Lactic acid | Lactide | Acetalde-hyde | Carbon monoxide |
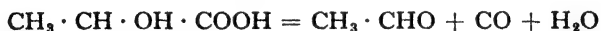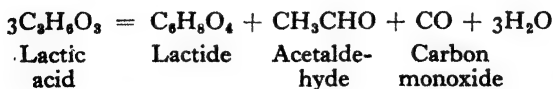
Lactide is obtained as colourless plates (m. pt. 120° C.). It is insoluble in water, but when boiled with water it is reconverted into lactic acid.

2. When heated with dilute sulphuric acid at 130° C. lactic acid is decomposed into aldehyde and formic acid:

$$CH_3CH(OH)COOH = CH_3CHO + H \cdot COOH$$
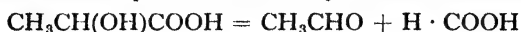
3. When heated with concentrated sulphuric acid it is decomposed into acetaldehyde and carbon monoxide:

$$CH_3CH(OH)COOH = CH_3CHO + CO + H_2O$$

4. Hydrobromic acid converts it into α-bromopropionic acid:

$$CH_3CH(OH)COOH + HBr = CH_3CHBrCOOH + H_2O$$
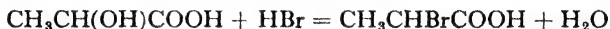
This reaction shows that the acid contains a *secondary alcohol* group $=CH \cdot OH$ (cf. isopropyl alcohol); this is also shown by its action with concentrated hydriodic acid, when the α-iodopropionic acid first formed is reduced by the excess of hydriodic acid to propionic acid.

5. On reduction with:

  (*a*) sodium amalgam and water, or
  (*b*) hydriodic acid and phosphorus, or
  (*c*) hydrogen and reduced nickel;

it is converted into propionic acid:

$$CH_3CH(OH)COOH + 2H = CH_3CH_2COOH + H_2O$$
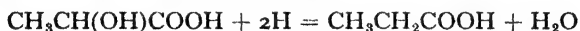
6. On oxidation with potassium permanganate, lactic acid behaves like a secondary alcohol and is converted into pyruvic acid (cf. isopropyl alcohol and acetone):

$$
\begin{array}{lll}
CH_3 & & CH_3 \\
| & & | \\
CH \cdot OH + O &=& C : O + H_2O \\
| & & | \\
COOH & & COOH \\
\text{Lactic acid} & & \text{Pyruvic acid}
\end{array}
$$
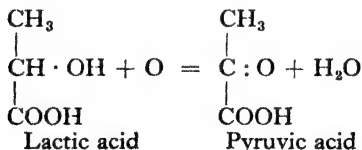
7. Lactic acid is a *mono*carboxylic acid and forms both metallic salts and esters, e.g.

Calcium lactate, $Ca(C_3H_5O_3)_2 \cdot 5H_2O$,
Zinc lactate, $Zn(C_3H_5O_3)_2 \cdot 3H_2O$.

These two salts are crystalline and dissolve in hot water.

Uses.—Lactic acid is used in the dyeing industry as an assistant in mordanting with potassium dichromate, especially in the dyeing of wool. Antimony lactate is also used in dyeing and calico printing. Lactic acid is used in the leather industry to remove lime and other calcium salts of organic acids from skins which have been dehaired in the lime vat. It is used in the manufacture of alcohol to prevent the growth of deleterious organisms. The iron and calcium salts are used in medicine.

Tests for Lactic Acid and Lactates are given in Chap. XXII, p. 531.

Ethyl lactate, $CH_3 \cdot CH(OH)CO \cdot O \cdot C_2H_5$, is a neutral liquid, but since it contains a $=CH \cdot OH$ group it yields metallic derivatives with alkali metals, and like other hydroxy compounds it interacts with acetyl chloride, giving ethyl acetyl lactate, $CH_3 \cdot CH(O \cdot C_2H_3O) \cdot CO \cdot O \cdot C_2H_5$, an ester of acetyl lactic acid.

$$
\begin{array}{ccccc}
CH_3 & & CH_3 & & CH_3 \\
| & (C_2H_5OH) & | & (CH_3COCl) & | \\
CHOH & \longrightarrow & CHOH & \longrightarrow & CH \cdot OOC \cdot CH_3 \\
| & & | & & | \\
COOH & & CO \cdot OC_2H_5 & & CO \cdot OC_2H_5 \\
\text{Lactic acid} & & \text{Ethyl lactate} & & \text{Ethyl acetyl lactate}
\end{array}
$$
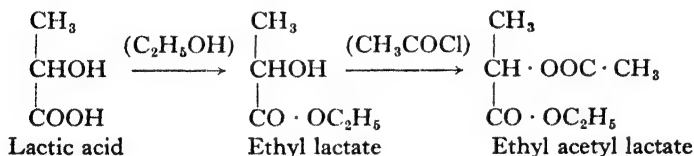
Sarcolactic Acid, Dextrolactic Acid, *d*-Ethylidene Lactic Acid, $CH_3 \cdot CHOH \cdot COOH$.

This acid is found in the juice of meat. Beef extracts such as Bovril and Liebig's extract of meat contain appreciable quantities of sarcolactic acid and may serve as a source of the acid. The extract is dissolved in water, and alcohol is added to precipitate the albuminous substances present. These are separated and the alcohol distilled off. The residue is then treated with mineral acid and the sarcolactic acid set free is extracted with ether.

Properties.—Colourless crystalline substance, m.pt. 25·5°C.

It is very hygroscopic, and forms salts and esters which are lævo-rotatory. The acid, however, is dextro-rotatory, and differs in this respect from the optically inactive acid obtained by fermentation. Its chemical properties are exactly similar to those of ordinary lactic acid.

Lævo-lactic Acid, *l*-Ethylidene Lactic Acid, $CH_3 \cdot CHOH \cdot COOH.$

This acid is obtained from the fermentation of cane sugar, by means of the *l*-lactic bacillus. It turns the plane of polarized light to the left through the same number of degrees as sarcolactic acid turns it to the right. Its salts and esters are dextro-rotatory. Its other physical properties such as melting-point, solubility, crystal system, and its chemical properties, are the same as those of sarcolactic acid.

The lactic acids are much stronger acids than propionic acid and hydracrylic acid.

Hydracrylic Acid, β-hydroxy-Propionic Acid, $CH_2OH \cdot CH_2 \cdot COOH.$

This acid is isomeric with the lactic acids but is not formed during lactic fermentation. It does not contain an asymmetric carbon atom; it is optically inactive and stereo-isomers do not exist. The hydroxyl group OH is attached to the β carbon atom.

Formation.—1. It may be synthesized from ethylene by treatment with hypochlorous acid, which yields ethylene chlorhydrin. The chlorhydrin is then converted into the corresponding nitrile, which is hydrolysed by boiling with an alkali:

$$\begin{array}{cccc}
& \text{(HOCl)} & \text{(KCN)} & \text{(KOH)} \\
CH_2 & CH_2 \cdot OH & CH_2 \cdot OH & CH_2OH \\
\| \quad \longrightarrow & | & \longrightarrow \quad | & \longrightarrow \quad | \\
CH_2 & CH_2Cl & CH_2CN & CH_2 \cdot COOH \\
\text{Ethylene} & \text{Ethylene or} & \text{Ethylene} & \text{Hydracrylic} \\
& \text{Glycol chlorhydrin} & \text{nitrile} & \text{acid}
\end{array}$$
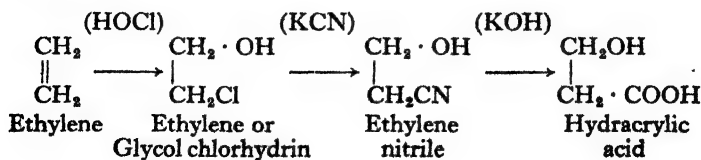
2. By boiling β-chloro-, bromo-, or iodo-propionic acid with water or weak aqueous alkalis, e.g. Ag_2O:

$$\begin{matrix} CH_2 \cdot I \\ | \\ CH_2 \cdot COOH \end{matrix} + HOH = \begin{matrix} CH_2OH \\ | \\ CH_2COOH \end{matrix} + HI$$

β-iodo-propionic   Hydracrylic
acid   acid
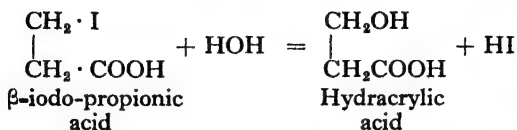
Properties.—It is a thick sour syrup. It differs from lactic acid as follows.

(*a*) On oxidation it yields carbonic and oxalic acids but not acetic acid:

$$CH_2OH \cdot CH_2COOH + 4O = (COOH)_2 + HO \cdot COOH + H_2$$

                                      Oxalic   Carbonic
                                          acid   acid
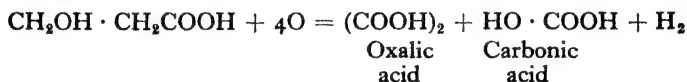
On oxidation with chromic acid it yields malonic acid:

$$\begin{matrix} CH_2OH \\ | \\ CH_2 \\ | \\ COOH \end{matrix} + 2O = \begin{matrix} COOH \\ | \\ CH_2 \\ | \\ COOH \end{matrix} + H_2O$$

Hydracrylic   Malonic
acid   acid
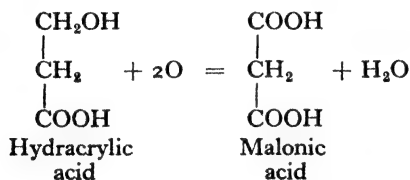
This proves the presence of the *primary alcohol* —CH_2OH group.

(*b*) It does not form an anhydride when heated alone or with moderately dilute sulphuric acid, but breaks up into water and acrylic acid, from which the name hydracrylic acid is derived:

$$\begin{matrix} CH_2OH \\ | \\ CH_2 \\ | \\ COOH \end{matrix} = \begin{matrix} CH_2 \\ || \\ CH \\ | \\ COOH \end{matrix} + H_2O$$

Hydracrylic   Acrylic
acid   acid
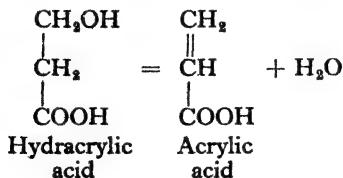
This reaction is characteristic of β-hydroxy-acids. Here only

the alcoholic properties (i.e. —CH_2OH group) are destroyed, the carboxyl —$COOH$ group remaining intact; but when lactic acid is heated the alcoholic and carboxylic hydroxyl groups are both involved, lactide being formed by the elimination of a molecule of water.

Its salts have a different amount of water of crystăllization, e.g.:

Zinc salt: $Zn(C_3H_5O_3)_2 \cdot 4H_2O$;
Calcium salt: $Ca(C_3H_5O_3)_2 \cdot 2H_2O$.

Constitution of the Hydroxy-propionic Acids.
—Lactic acid and hydracrylic acid are both hydroxy-monocarboxylic acids of molecular composition $C_3H_6O_3$, and two formulæ are possible, namely:

I	II
$CH_3CH(OH) \cdot COOH$	$CH_2OH\ CH_2COOH$
$CH_3CH =$ Ethylidene group	$-CH_2CH_2 -$ Ethylene group
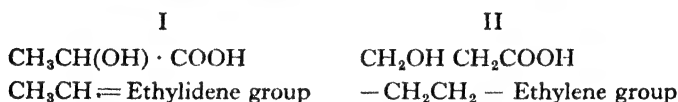
Formula I is established as that of lactic acid, for the following reasons:

(*a*) When aldehyde is treated with hydrocyanic acid, direct combination occurs; on boiling the product with hydrochloric acid, lactic acid is obtained:

$$\underset{\substack{| \\ \text{CHO}}}{\text{CH}_3} \xrightarrow{\text{(HCN)}} \underset{\substack{| \\ \text{CH} \cdot \text{OH} \cdot \text{CN}}}{\text{CH}_3} \xrightarrow{\text{(HCl)}} \underset{\substack{| \\ \text{CHOH} \cdot \text{COOH}}}{\text{CH}_3}$$
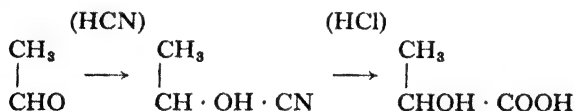
i.e. lactic acid contains a methyl (—CH_3) radicle, a hydroxyl (OH) radicle, and a carboxyl (—$COOH$) radicle.

(*b*) The methods of formation already stated, and the formation of a lactide, suggest this formula.

(*c*) It contains a secondary —CHOH alcohol group (proved by the formation of α-bromopropionic acid and pyruvic acid).

Formula II, containing a primary —CH_2OH alcohol group, is that of hydracrylic acid; this is fully borne out by the synthesis of hydracrylic acid from ethylene and by its properties.

Lactones.

The salts of α- and β-mono-hydroxy monobasic acids when treated with a mineral acid set free the corresponding acid, e.g.:

$$CH_2OH \cdot COONa + HCl = CH_2OH \cdot COOH + NaCl$$

<div align="center">Sodium glycollate   Glycollic acid or
α-hydroxy-acetic acid</div>

$$CH_3 \cdot CH \cdot OH \cdot COONa + HCl = CH_3 \cdot CH \cdot OH \cdot COOH + NaCl$$

<div align="center">Sodium lactate   Lactic acid or
α-hydroxy-propionic acid</div>
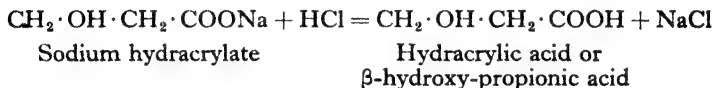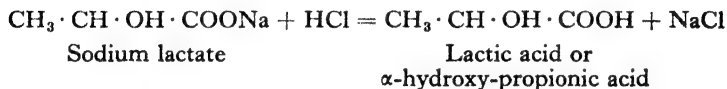
$$CH_2 \cdot OH \cdot CH_2 \cdot COONa + HCl = CH_2 \cdot OH \cdot CH_2 \cdot COOH + NaCl$$

<div align="center">Sodium hydracrylate   Hydracrylic acid or
β-hydroxy-propionic acid</div>
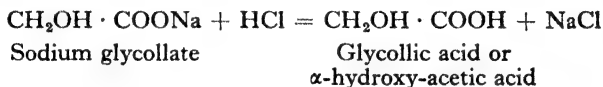
The salts of γ-, δ-, and higher hydroxy monobasic acids, however, differ from those of the α- and β-hydroxy-acids in that when they are treated with a mineral acid a neutral compound called a **lactone** is precipitated. This compound is formed from the acid by the loss of the elements of water. The changes which γ-hydroxy-butyric acid undergoes may be represented as follows:

$$
\begin{array}{ccccc}
& (NaOH) & & (HCl) & \\
CH_2 \cdot CH_2(OH) & & CH_2 \cdot CH_2(OH) & & CH_2 \cdot CH_2 \\
| & \rightarrow & | & \rightarrow & | \quad\rangle O + NaCl + H_2O \\
CH_2 \cdot COOH & & CH_2 \cdot COONa & & CH_2 \cdot CO \\
\text{γ-hydroxy-} & & \text{Sodium γ-hydroxy-} & & \text{γ-butyro-lactone} \\
\text{butyric acid} & & \text{butyrate} & & \text{or Butanolid}
\end{array}
$$
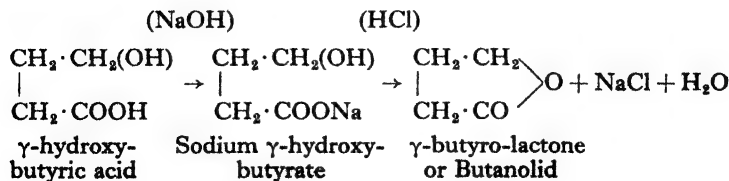
Similar compounds may be obtained with other γ- and δ-acids, e.g.

$CH_3 \cdot CHOH \cdot CH_2 \cdot CH_2 \cdot COOH$ gives

$$\begin{array}{l} CH_3 \cdot CH\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!\rceil \\ \quad| \qquad\qquad\qquad O; \\ CH_2 \cdot CH_2 \cdot CO\!-\!\rfloor \end{array}$$

γ-hydroxy-valeric acid

γ-valero-lactone

$CH_2(OH) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$ gives

$$\begin{array}{l} CH_2 \cdot CH_2 \!\!-\!\!\!\searrow \\ \quad| \qquad\qquad\quad O \\ CH_2 \cdot CH_2 \cdot CO\!\!\nearrow \end{array}$$

δ-hydroxy-valeric acid

δ-valero-lactone
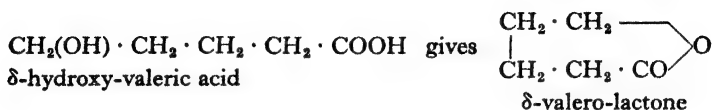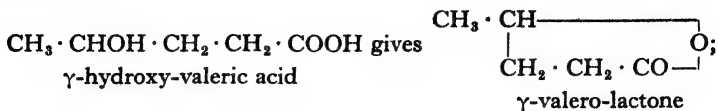
A lactone or inner ester may be defined as an anhydride of a hydroxy-acid.

Lactones are usually liquids and are neutral substances, but form salts of the corresponding hydroxy-acids when they are boiled for some time with bases in solution.

The γ-lactones have a faint aromatic odour and are readily soluble in alcohol or ether. With hydrobromic acid they form brominated fatty acids and with ammonia either amino-acids or amides.

The formation of lactones is no doubt due to the space arrangements of the carbon atoms. Since the linkages of the carbon atoms in the so-called straight chains diverge at an angle of 109°, a carbon compound containing three or more carbon atoms has the tendency to form a closed chain, as follows:

γ-hydroxy-butyric acid γ-butyro-lactone
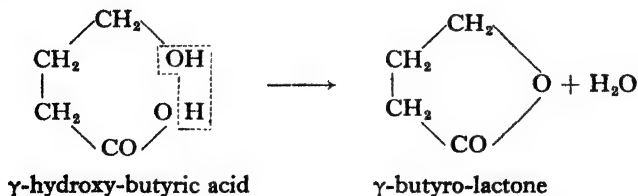
The two hydroxyl groups condense with elimination of one molecule of water to form the lactone.

Lactides.

The α-hydroxy-acids, e.g. glycollic acid and lactic acid, form **lactides** by the condensation of two molecules of the acid with the elimination of two molecules of water. This condensation is brought about either by distillation in a vacuum or by direct heating (cf. pp. 247, 267).
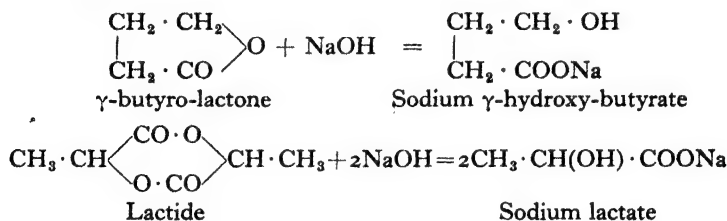
The β-hydroxy-acids, e.g. hydracrylic acid, form unsaturated acids by the loss of one molecule of water from one molecule of the acid (p. 271). They do not form anhydrides.

Both lactides and lactones have properties like those of esters. They are neutral substances, insoluble in dilute alkalis, and undergo hydrolysis with the formation of an alkali salt:

$$\begin{array}{l} CH_2 \cdot CH_2 \\ | \Big\rangle O + NaOH \\ CH_2 \cdot CO \end{array} = \begin{array}{l} CH_2 \cdot CH_2 \cdot OH \\ | \\ CH_2 \cdot COONa \end{array}$$

γ-butyro-lactone $\qquad$ Sodium γ-hydroxy-butyrate

$$CH_3 \cdot CH\begin{array}{c} CO \cdot O \\ \Big\langle \Big\rangle \\ O \cdot CO \end{array} CH \cdot CH_3 + 2NaOH = 2CH_3 \cdot CH(OH) \cdot COONa$$

Lactide $\qquad\qquad\qquad\qquad\qquad$ Sodium lactate

DIHYDRIC ALCOHOLS OR GLYCOLS

These may be regarded as dihydroxy derivatives of the paraffins. They have the general formula

$$C_nH_{2n}(OH)_2$$
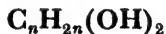
Ethylene glycol is the simplest member of this class:

Ethylene glycol, $\qquad$ $\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$
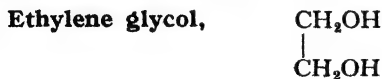
Formation.—1. By hydrolysis of ethylene dibromide (i.e. a dihalogen compound) with aqueous potassium carbonate:

$$C_2H_4Br_2 + 2HOH \rightleftharpoons C_2H_4(OH)_2 + 2HBr$$
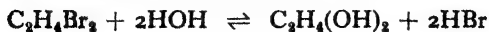
2. By careful oxidation of ethylene (i.e. an olefine) with very dilute potassium permanganate:

$$CH_2{=}CH_2 + O + HOH = OH{-}CH_2{-}CH_2{-}OH$$
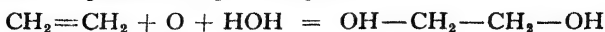
Properties.—Colourless viscous liquid, sp. gr. 1·125, b. pt. 197° C. Sweetish taste; soluble in water and alcohol but not in ether.

Reactions.—1. It acts as an alcohol, forming alcoholates, e.g.:

Sodium glycol, $C_2H_4OH \cdot ONa$; Disodium glycol, $C_2H_4(ONa)_2$

2. It forms esters with acids, e.g.:

Mono-acetate, $C_2H_4OH \cdot OOC \cdot CH_3$; Di-acetate, $C_2H_4(OOC \cdot CH_3)_2$

3. On oxidation it yields (*a*) aldehydes, e.g. glycollic aldehyde and glyoxal; (*b*) acids, e.g. glycollic, glyoxylic and oxalic acids.

4. On chlorination it yields ethylene dichloride, $C_2H_4Cl_2$.

For Practice.—Write equations for the reactions stated above.

QUESTIONS

1. Describe a method for the preparation of lactic acid. The lactic acid obtained from glucose is described as " optically inactive ", whereas that which occurs in muscle juice is " dextro-rotatory ". Explain the significance of these terms and their bearing on the constitution of lactic acid.   (*Pre. Med.*)

2. Write the names and constitutional formulæ for any two compounds which possess the empirical formula CH_2O. Describe the reactions of one of these compounds and show that expression is given to these reactions by the constitutional formula.

(*Cambridge Higher School Cert.*)

3. Give a list of the principal naturally occurring aliphatic monohydroxy acids with their constitution. Write notes on the chief points of interest connected with any two of these acids.

(*II. M.B., London.*)

4. By what sequence of reactions may ethylene glycol be prepared from ethyl alcohol?

Show by means of formulæ the oxidation products of ethylene glycol, and name them.

5. Write down the structural formulæ for three aliphatic organic compounds having the molecular formula $C_3H_6O_3$, and describe briefly the reactions by which you would distinguish them. (*Chemists and Druggists Qual.*)

6. Describe the isolation of any one amino-acid from a naturally occurring protein. How would you prove that it contains both carboxyl and amino groups? (*II. M.B., London.*)

7. Write down the names and structural formulæ of the various possible isomers of the formula $C_3H_6O_3$. Explain carefully how these isomers could be distinguished from each other.

(*Phar. Chem. Qual.*)

8. How many lactic acids are known and how may the structure of lactic acid be established? What are lactones?

(*Chemists and Druggists Qual.*)

9. Write the structural formula for three substances having the empirical formula CH_2O and belonging to three different classes of organic compounds. Describe the general reactions by which these three classes are distinguished and indicate briefly how you would identify the three substances you have chosen.

(*Chemists and Druggists Qual.*)

10. Give two methods for the preparation of lactic acid. Briefly describe the physical and chemical properties of this substance and mention some of its uses. (*Phar. Chem. Qual.*)

11. How is glycine prepared, starting with acetic acid? What is the action of formaldehyde on glycine? Give one method for differentiating between glycine and acetamide.

12. Write equations for a series of reactions by which lactic acid might be prepared from ethyl alcohol. What evidence goes to show that lactic acid contains (*a*) a hydroxyl group, (*b*) a carboxyl group? Explain how a study of the isomerism of lactic acid leads to a knowledge of the directions of the four valencies of the carbon atom. (*Inter B.Sc., London.*)

Polybasic Acids and their Derivatives

The polybasic acids contain two or more carboxyl radicles. The following four groups will be discussed:

> A. Saturated dibasic acids.
> B. Unsaturated dibasic acids.
> C. Hydroxy dibasic acids.
> D. Monohydroxy tribasic acids.

A. Saturated Dibasic Acids

The saturated dibasic acids have the general formula

$$C_nH_{2n-2}O_4 \quad \text{or} \quad C_nH_{2n}(COOH)_2$$

and may be regarded as dicarboxylic acids of the paraffins. Examples include:

Oxalic acid $COOH \cdot COOH$
Malonic acid $COOH \cdot CH_2 \cdot COOH$, from Methane CH_4
Succinic acid $COOH \cdot CH_2 \cdot CH_2 \cdot COOH$, from Ethane $CH_3 \cdot CH_3$

These acids can form both acid and normal salts, and two series of chlorides, esters, amides, &c. The above acids are white crystalline solids soluble in water. On heating they yield either a monobasic acid or an anhydride.

**Oxalic Acid,** $(COOH)_2 \cdot 2H_2O$.

Occurrence.—As acid potassium oxalate in plants of the genus *Oxalis*, such as wood sorrel (*Oxalis acetosella*); as

the sodium salt in plants of the genus *Salicornia*; as the ammonium salt in guano and as the calcium salt in many plants, e.g. rhubarb root, and in urinary calculi.

Scheele (1776) was the first to prepare oxalic acid in the laboratory by the action of nitric acid on sugar.

Formation.

1. By passing carbon dioxide over sodium heated to 360° C.:

$$2CO_2 + 2Na = (COONa)_2$$
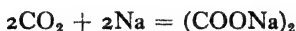
2. *Commercial methods.*

A. Synthetic method: by heating sodium formate either alone or with sodium carbonate to 360° C.:

$$\begin{matrix} H \cdot COONa \\ + \\ H \cdot COONa \end{matrix} = \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2$$

Sodium formate   Sodium oxalate

$$H \cdot COONa + Na_2CO_3 = Na_2C_2O_4 + NaOH$$
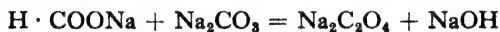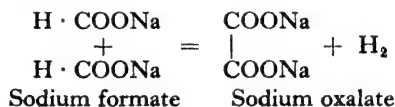
The acid is liberated from its salts by treatment with mineral acids.

B. Natural method: by heating cellulose in the form of pine sawdust with a mixture of caustic alkalis to 250° C. in iron pans. The heating must be so conducted that the sawdust does not char.

The resulting brown mass is extracted with hot water and filtered and the alkali oxalates are precipitated with milk of lime:

$$(COONa)_2 + (COOK)_2 + 2Ca(OH)_2$$
$$= 2NaOH + 2KOH + 2Ca(COO)_2$$
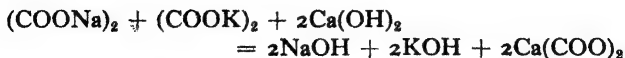
The precipitated calcium oxalate is filtered off and the alkaline filtrate is used again. The calcium oxalate is next decomposed with the requisite quantity of dilute sulphuric

acid; calcium sulphate is deposited and the solution left, containing the oxalic acid, is evaporated and allowed to crystallize. The pure acid is obtained by repeated recrystallization.

This method is being displaced by the synthetic process.

3. By allowing an aqueous solution of cyanogen (p. 327) to stand for some time; other products are, however, formed at the same time:

$$\begin{matrix} CN \\ | \\ CN \end{matrix} + 4H_2O = \begin{matrix} COONH_4 \\ | \\ COONH_4 \end{matrix}$$

Cyanogen   Ammonium
                          oxalate
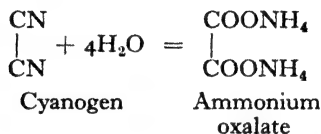
The acid is liberated from the ammonium salt by treatment with sulphuric acid.

The formation of oxalic acid from carbon dioxide, formic acid, or cyanogen is important and is utilized as a means of synthesizing oxalic acid from its elements, since each of these compounds may be obtained from its elements.

4. By the oxidation of certain organic substances, e.g. alcohol, glycol, cane sugar, fats, starch, cellulose, with nitric acid:

$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + 2O_2 = \begin{matrix} COOH \\ | \\ COOH \end{matrix} + 2H_2O$$

Glycol   Oxalic acid
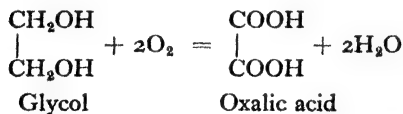
The pure acid is obtained by oxidizing cane sugar with concentrated nitric acid:

$$C_{12}H_{22}O_{11} + 9O_2 = 6(COOH)_2 + 5H_2O$$

Cane sugar   Oxalic acid
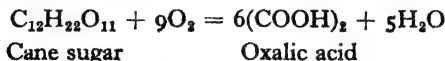
Experiment.—Weigh out into a large flask about 50 to 60 gm. of cane sugar, then add cautiously 200 c.c. of concentrated nitric acid. Heat this mixture on the water bath until

the copious brown fumes evolved have disappeared. If the reaction becomes too violent cool the flask under the tap. Allow the liquid to stand overnight; crystals of oxalic acid will be deposited. These are separated by filtration and purified by recrystallization from water.

Properties.—White crystalline solid containing two molecules of water of crystallization. It loses water at 100° C. and then melts at 189·5° C. The monoclinic crystals effloresce slowly in the air. Oxalic acid decomposes above 200° C. into oxides of carbon, formic acid and water:

$$2(COOH)_2 = CO + 2CO_2 + H \cdot COOH + H_2O$$

It is readily soluble in hot water, from which it may be crystallized, and to a lesser degree in alcohol. The anhydrous acid is obtained by heating the crystals in a steam oven. It is very hygroscopic, and hence can be employed as a powerful dehydrating agent. Oxalic acid in solution has an acid reaction, and can react with alkalis, carbonates and certain metallic oxides to form salts.

Oxalic acid is **poisonous**.

Reactions 1.—As a **dibasic acid.** It forms both normal and acid salts and two series of esters, known as oxalates. Examples:

Salts:

normal:
$$\begin{matrix} COOK \\ | \\ COOK \end{matrix} \cdot H_2O \quad \begin{matrix} \text{Potassium} \\ \text{oxalate;} \end{matrix} \qquad \begin{matrix} COO \\ | \\ COO \end{matrix}\!\!>\!\!Ca \quad \begin{matrix} \text{Calcium} \\ \text{oxalate.} \end{matrix}$$

acid:
$$\begin{matrix} COOK \\ | \\ COOH \end{matrix} \quad \begin{matrix} \text{Acid potassium} \\ \text{oxalate;} \end{matrix} \qquad \begin{matrix} COOH \\ | \\ COOH \end{matrix} \begin{matrix} COOK \\ | \\ COOH \end{matrix} \cdot 2H_2O \quad \begin{matrix} \text{Potassium} \\ \text{tetroxalate.} \end{matrix}$$

Esters:

$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} \quad \begin{matrix} \text{Diethyl} \\ \text{oxalate;} \end{matrix} \qquad \begin{matrix} COOC_2H_5 \\ | \\ COOH \end{matrix} \quad \begin{matrix} \text{Mono-ethyl} \\ \text{oxalate.} \end{matrix}$$

2. As a **reducing agent.**—It can reduce warm (60° C.) potassium permanganate or manganese dioxide in acid solution, discharging the pink colour of the permanganate and being oxidized to carbon dioxide:

$$(COOH)_2 + O = 2CO_2 + H_2O;$$

$$5(COOH)_2 + 2KMnO_4 + 3H_2SO_4$$
$$= K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$
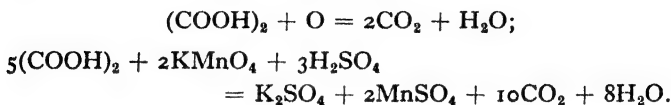
This reaction is used in volumetric analysis, the oxalic acid being employed to standardize solutions of potassium permanganate.

Nitric acid and chlorine are not reduced by oxalic acid.

The reducing properties of oxalic acid are employed to precipitate gold from its solutions.

3. It is decomposed by concentrated sulphuric acid into carbon monoxide and carbon dioxide. The sulphuric acid acts as a dehydrating agent in the reaction:

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} - HOH = CO + CO_2$$
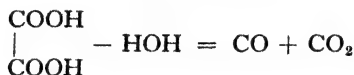
4. It is reduced to glycollic acid by nascent hydrogen:

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} + 4H = \begin{array}{l} CH_2OH \\ | \\ COOH \end{array} + H_2O$$
$$\text{Glycollic acid}$$
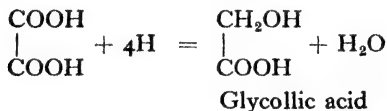
5. It reacts with phosphorus pentachloride to form oxalyl chloride:

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} + 2PCl_5 = \begin{array}{l} COCl \\ | \\ COCl \end{array} + 2POCl_3 + 2HCl$$
$$\text{Oxalyl chloride}$$
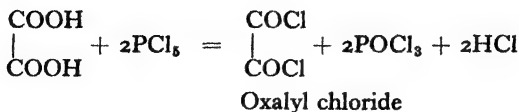
Oxalyl chloride is a colourless pungent-smelling liquid (b. pt. 70° C.).

Uses.—Oxalic acid is used for whitening leather; in laundries to remove ink stains and iron mould from cloth; in bleaching stearin and straw (hats); for dissolving Prussian blue in ink manufacture; for metal polishing powders; in analytical chemistry as a reagent; as a mordant for cloth printing and dyeing; and in photography.

Oxalates.—The alkali oxalates are readily soluble in hot water, but most of the other oxalates are either only sparingly soluble or insoluble. The soluble salts are **poisonous.**

Ammonium oxalate, $(COONH_4)_2 \cdot H_2O$, when carefully heated is decomposed, yielding oxamide:

$$\begin{array}{ccc} COONH_4 & & CONH_2 \\ | & = & | & + \; 2H_2O \\ COONH_4 & & CONH_2 \end{array}$$
$$\text{Ammonium oxalate} \qquad \text{Oxamide}$$

Potassium oxalate, $(COOK)_2 \cdot H_2O$, is readily soluble in water and is used to prevent coagulation of the blood (clotting), by precipitating the calcium present as calcium oxalate.
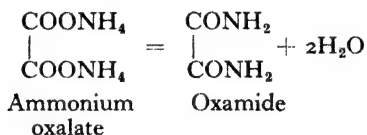
Potassium hydrogen oxalate, (KHC_2O_4), is more sparingly soluble than the normal salt and occurs in many plants. It is used as a detergent.

Potassium tetroxalate, $(COOH)_2 \cdot C_2O_4HK \cdot 2H_2O$, known as Salts of Sorrel or Salts of Lemon, can be used to remove ink stains and iron mould; it reacts with the iron present to form soluble iron-potassium oxalate. It is used as a detergent and as a reliable standard in acidimetry.

Calcium oxalate, $(COO)_2Ca$, is found in plants. It is insoluble in water and in acetic acid, a fact utilized in chemical analysis. It is soluble in dilute hydrochloric acid and in nitric acid.

Ferrous oxalate, $(COO)_2Fe \cdot 2H_2O$, is obtained as an insoluble yellow precipitate when ferrous sulphate is added to a solution of a soluble oxalate.

Potassium ferrous oxalate, $(COOK)_2 \cdot (COO)_2Fe \cdot H_2O$, has strong reducing properties, and hence is used as a developer in photography. It is made by mixing solutions containing corresponding amounts of ferrous sulphate and potassium oxalate.

Silver oxalate, $(COOAg)_2$, is obtained as a very sparingly soluble precipitate when silver nitrate is added to a solution of a neutral oxalate. It is soluble in dilute nitric acid. The dry salt explodes when rapidly heated, leaving a residue of silver.

Esters of Oxalic Acid include

Dimethyl oxalate, $\begin{vmatrix} COOCH_3 \\ COOCH_3 \end{vmatrix}$, a solid (m. pt. 54° C., b. pt. 162° C.);

Di-ethyl oxalate, $\begin{vmatrix} COOC_2H_5 \\ COOC_2H_5 \end{vmatrix}$, a colourless liquid (b. pt. 186° C.).

These esters can be obtained by distilling the appropriate alcohol with anhydrous oxalic acid.

Both these esters have an aromatic odour and can be readily hydrolysed in the cold. When they are heated with alcoholic potash, partial hydrolysis takes place; potassium ethyl oxalate $(C_2H_5 \cdot OOC \cdot COOK)$ is formed. These esters are converted into oxamide when heated with concentrated ammonia:

$$CO \cdot \boxed{OC_2H_5 \quad H} \cdot NH_2 \qquad CO \cdot NH_2$$
$$\underset{\displaystyle \text{Di-ethyl oxalate}}{\Big|} \underset{+}{} \quad = \quad \underset{\displaystyle \text{Oxamide}}{\Big|} \quad + \quad 2C_2H_5OH$$
$$CO \cdot \boxed{OC_2H_5 \quad H} \cdot NH_2 \qquad CO \cdot NH_2$$
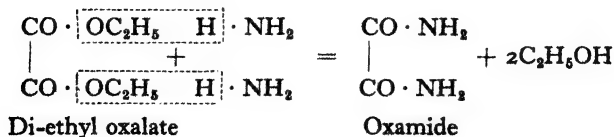
Oxamide is a white crystalline substance, m. pt. 418° C. Its reactions with phosphorus pentoxide and on hydrolysis by alkalis are of interest; cyanogen (p. 327) and oxalic acid are formed by the elimination and addition of two molecules of water respectively.

$$
\begin{array}{l}
\qquad\qquad (P_2O_5) \\
CO \cdot NH_2 \; - \; 2H_2O \; \nearrow \; CN{-}CN \\
\qquad\qquad\qquad\qquad\qquad\quad \text{Cyanogen} \\
CO \cdot NH_2 \; + \; 2H_2O \; \searrow \; 2NH_3 + (COOH)_2 \\
\qquad\;\; (\text{Hydrolysis}) \qquad\quad \text{Oxalic acid}
\end{array}
$$
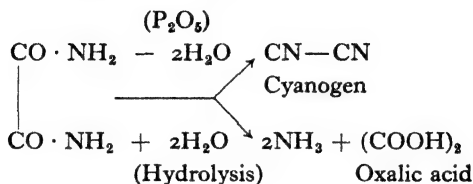
Tests for Oxalic Acid and Oxalates.

The reactions with concentrated sulphuric acid, potassium permanganate, silver nitrate, and calcium chloride serve as tests for these compounds. (See Chapter XXII, p. 530.)

Carbonic Acid, $(HO \cdot CO \cdot OH)$.

Although carbonic acid is not a dicarboxylic acid it is included here as a dibasic acid. The two —OH groups can be displaced by two chlorine atoms to form carbonyl chloride or phosgene, $COCl_2$. This compound is also formed by the direct union of carbon monoxide and chlorine in sunlight. An important derivative of carbonic acid is urea or carbamide, $CO(NH_2)_2$ (Chapter XII).

Malonic Acid, $CH_2\!\!\begin{array}{l}{\nearrow COOH}\\{\searrow COOH,}\end{array}$
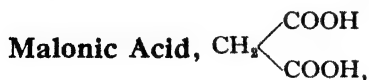
occurs in beetroot as the calcium salt.

Formation.

1. By heating a solution of potassium chloracetate with

potassium cyanide. The potassium cyano-acetate formed is
then hydrolysed by boiling with hydrochloric acid:

$$\begin{matrix} CH_2Cl \\ | \\ COOK \end{matrix} + KCN = \begin{matrix} CH_2CN \\ | \\ COOK \end{matrix} + KCl;$$

$$CH_2\Big\langle\begin{matrix} CN \\ COOK \end{matrix} + 3HOH = CH_2\Big\langle\begin{matrix} COOH \\ COOH \end{matrix} + NH_3 + KOH.$$

<div align="center">Potassium
cyano-acetate   Malonic acid</div>

2. By oxidizing malic acid with chromic acid:

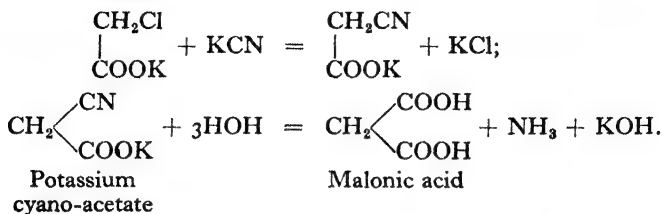$$CH_2\Big\langle\begin{matrix} COOH \\ CH(OH)\cdot COOH \end{matrix} + 2O = CH_2\Big\langle\begin{matrix} COOH \\ COOH \end{matrix} + CO_2 + H_2O$$

<div align="center">Malic acid   Malonic acid</div>
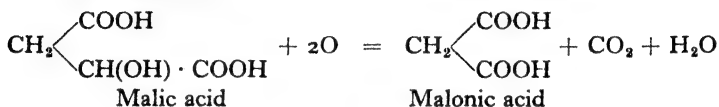
Properties.—It is a white crystalline solid (m. pt. 132° C.),
soluble in water, alcohol and ether. It loses carbon dioxide
at 150° C., acetic acid being formed:

$$CH_2\Big\langle\begin{matrix} COOH \\ COOH \end{matrix} = CH_3COOH + CO_2$$

This reaction is typical of all dicarboxylic acids and serves
to illustrate the instability of two carboxyl groups attached
to the same carbon atom. The following rule should be
memorized by the student:

**All dicarboxylic acids which have two carboxyl
groups attached to the same carbon atom decom-
pose when heated above their melting-points into a
monocarboxylic acid and carbon dioxide.**

Malonic acid forms two series of salts and esters, known
as *malonates*.

Ethyl Malonate, $CH_2\Big\langle\begin{matrix} CO\cdot O\cdot C_2H_5 \\ CO\cdot O\cdot C_2H_5, \end{matrix}$
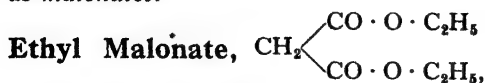
is the chief derivative of malonic acid, and is known as
Malonic Ester.

Formation.

By passing hydrogen chloride into a solution of cyano-acetic acid in absolute alcohol:

$$CH_3 \cdot COOH \xrightarrow{(Cl)} CH_2 \begin{cases} Cl \\ COOH \end{cases} \xrightarrow{(HCN)} CH_2 \begin{cases} CN \\ COOH \end{cases}$$

Acetic acid   Chloracetic acid   Cyano-acetic acid

$$\xrightarrow{(C_2H_5OH)} CH_2 \begin{cases} CO \cdot OC_2H_5 \\ CO \cdot OC_2H_5 \end{cases}$$
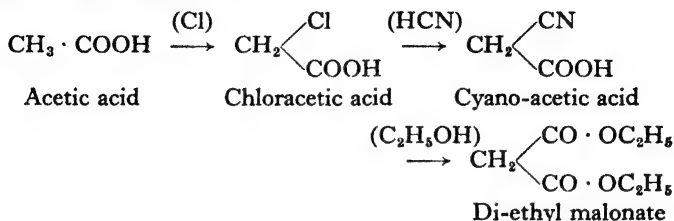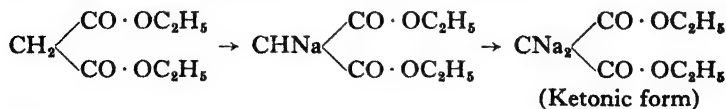
Di-ethyl malonate

It is a colourless liquid with a faint aromatic odour, b. pt. 198° C. Its properties are similar to those of aceto-acetic ester (p. 134). Its reactions are of considerable importance in organic synthesis.

Reactions.

.1. Like aceto-acetic ester, malonic ester contains the group —CO—CH$_2$—CO—. The methylene group —CH$_2$— under the influence of the carbonyl —CO— groups contains hydrogen atoms which are replaceable by sodium atoms, and these mono- and di-sodium derivatives, when heated with an alkyl halide, yield compounds in which the alkyl group is attached directly to the central carbon atom.

In order to obtain the sodium derivatives the malonic ester is dissolved in alcohol and boiled under a reflux condenser with the requisite quantity of sodium:

$$CH_2 \begin{cases} CO \cdot OC_2H_5 \\ CO \cdot OC_2H_5 \end{cases} \rightarrow CHNa \begin{cases} CO \cdot OC_2H_5 \\ CO \cdot OC_2H_5 \end{cases} \rightarrow CNa_2 \begin{cases} CO \cdot OC_2H_5 \\ CO \cdot OC_2H_5 \end{cases}$$

(Ketonic form)

or

$$\begin{matrix} C_2H_5O \\ NaO \end{matrix} C = C = C \begin{matrix} O \cdot C_2H_5 \\ ONa \end{matrix} \quad \text{(Di-enolic form)}$$

Ethyl sodiomalonate
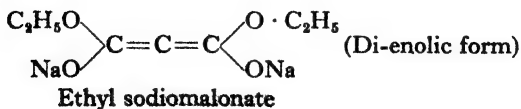
2. (a) The mono-sodium derivative when condensed with an alkyl halide yields a higher dibasic acid:

$$\text{NaCH}\begin{cases} \text{CO} \cdot \text{OC}_2\text{H}_5 \\ \text{CO} \cdot \text{OC}_2\text{H}_5 \end{cases} + \text{CH}_3\text{I} = \text{CH}_3 \cdot \text{CH}\begin{cases} \text{CO} \cdot \text{OC}_2\text{H}_5 \\ \text{CO} \cdot \text{OC}_2\text{H}_5 \end{cases} + \text{NaI}$$

Methyl malonic ester
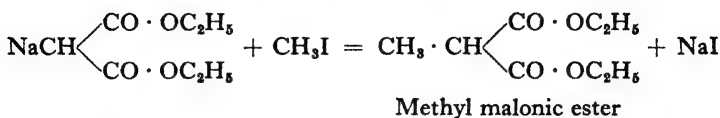
This ester on hydrolysis is converted into the higher dibasic acid:

$$\text{CH}_3 \cdot \text{CH}\begin{cases} \text{CO} \cdot \text{OC}_2\text{H}_5 \\ \text{CO} \cdot \text{OC}_2\text{H}_5 \end{cases} + 2\text{HOH}$$

$$= \text{CH}_3 \cdot \text{CH}\begin{cases} \text{COOH} \\ \text{COOH} \end{cases} + 2\text{C}_2\text{H}_5\text{OH}$$

Methyl malonic acid
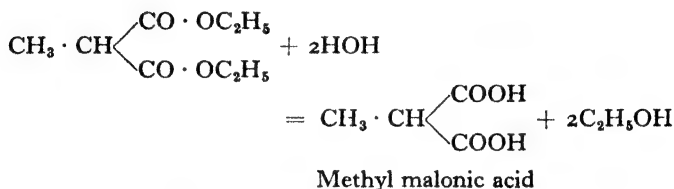
and so on for higher alkyl radicles.

(b) The di-sodium derivative when condensed with a di-halogen compound forms a ring or closed-chain compound:
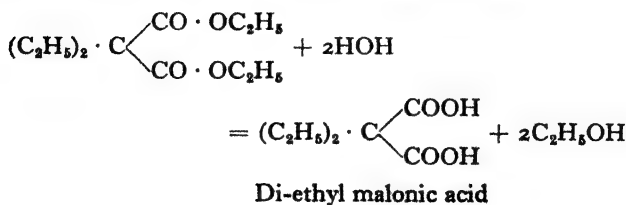
$$\text{Na}_2\text{C}\begin{cases} \text{CO} \cdot \text{OC}_2\text{H}_5 \\ \text{CO} \cdot \text{OC}_2\text{H}_5 \end{cases} + \begin{matrix} \text{CH}_2\text{Br} \\ | \\ \text{CH}_2\text{Br} \end{matrix} = \begin{matrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{matrix}\text{C}\begin{cases} \text{CO} \cdot \text{OC}_2\text{H}_5 \\ \text{CO} \cdot \text{OC}_2\text{H}_5 \end{cases} + 2\text{NaBr}$$

Ethylene
Dibromide
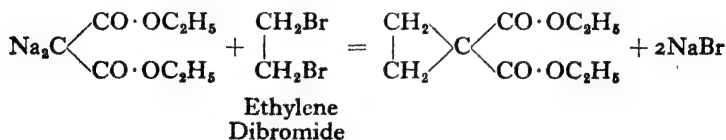
The di-sodium compound also forms alkyl-substituted esters, which on hydrolysis yield higher dibasic acids:

$$(\text{C}_2\text{H}_5)_2 \cdot \text{C}\begin{cases} \text{CO} \cdot \text{OC}_2\text{H}_5 \\ \text{CO} \cdot \text{OC}_2\text{H}_5 \end{cases} + 2\text{HOH}$$

$$= (\text{C}_2\text{H}_5)_2 \cdot \text{C}\begin{cases} \text{COOH} \\ \text{COOH} \end{cases} + 2\text{C}_2\text{H}_5\text{OH}$$

Di-ethyl malonic acid

3. Formation of higher fatty acids. The higher dibasic acids described above, when heated, yield higher fatty acids:

$$CH_3 \cdot CH{\Large<}^{COOH}_{COOH} = CH_3 \cdot CH_2 \cdot COOH + CO_2;$$
$$\text{Propionic acid}$$

$$(C_2H_5)_2 \cdot C{\Large<}^{COOH}_{COOH} = {}^{C_2H_5}_{C_2H_5}{\Large>}CH \cdot COOH + CO_2.$$
$$\text{Di-ethyl acetic acid}$$
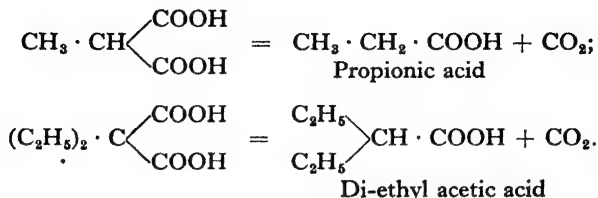
By this means the higher homologues can be prepared from acetic acid.

Keto-enolic Tautomerism.

It has been mentioned above that the di-sodium derivatives of malonic ester exist in two forms, namely, the **ketonic form** and the **enolic form**.

The ketonic form contains a ketone group —CO— which is not apparent in the enolic form; hence this is a special type of tautomerism, known as **Keto-enolic tautomerism.**

Keto-enolic tautomerism may be defined as a special type of tautomerism in which a compound contains a double bond, the position of which can be changed owing to the presence of an oscillatory hydrogen atom.

The change of position of the double bond is known as **desmotropism.** If the compound has one oscillatory hydrogen atom which changes the position of one double bond, the non-ketonic form is said to be **mono-enolic**: if two oscillatory hydrogen atoms are present, changing the position of two double bonds, the non-ketonic form is **di-enolic** and so on. The ketonic and enolic forms differ as regards solubility, physical and chemical characteristics.
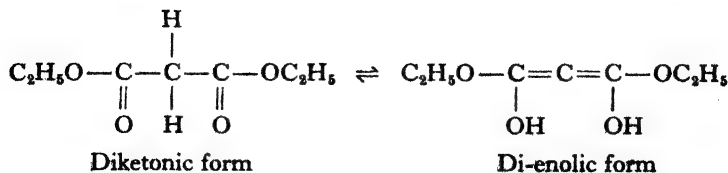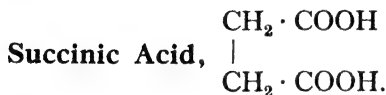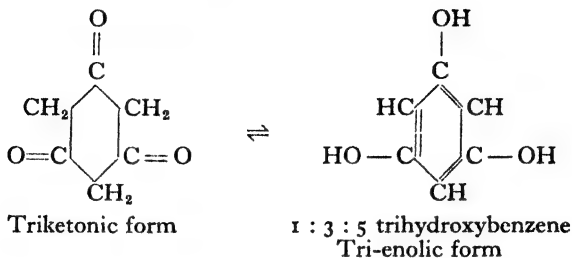
Examples include:

A. Aceto-acetic ester.

$$CH_3 - C - CH_2COOC_2H_5 \rightleftharpoons CH_3C(OH) = CH \cdot COOC_2H_5$$
$$\underset{\displaystyle O}{\overset{\displaystyle \|}{}}$$
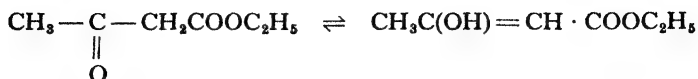
Properties:

Ketonic form	Enolic form
1. Insoluble in caustic alkalis.	1. Soluble in caustic alkalis.
2. Crystals melt at $-39°$ C.	2. Crystals obtained only by cooling in liquid air.
3. Reacts with $NaHSO_3$, HCN and NH_2OH as a ketone.	3. Does not react as a ketone.
4. Reacts with PCl_5 and NH_3 as a ketone.	4. PCl_5 forms $CH_3CCl = CHCOOH$, chloro-crotonic acid. NH_3 forms $CH_3C(NH_2) = CHCOOH$, amino-crotonic acid.
5. $FeCl_3$: no colour.	5. $FeCl_3$: violet coloration.
6. Br_2: no combination.	6. Br_2: combines immediately.

B. Malonic ester exists almost entirely in the ketonic form, although its derivatives exhibit keto-enolic tautomerism.

$$C_2H_5O - C - \overset{\displaystyle \overset{H}{|}}{C} - C - OC_2H_5 \rightleftharpoons C_2H_5O - C = C = C - OC_2H_5$$
$$\underset{O \quad H \quad O}{\overset{\| \quad | \quad \|}{}} \qquad \underset{OH \qquad OH}{\overset{| \qquad |}{}}$$

       Diketonic form   Di-enolic form

C. **Phloroglucinol** (p. 420).

Triketonic form   ⇌   1 : 3 : 5 trihydroxybenzene
Tri-enolic form

Succinic Acid, $\begin{array}{l} CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH. \end{array}$
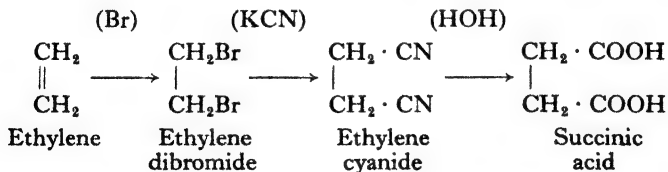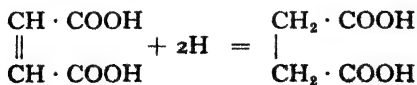
The name comes from the Latin *succinum*, amber, as the acid occurs in amber. It is also found in resins, urine, blood grapes, &c.
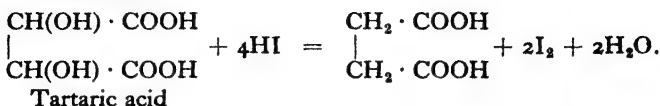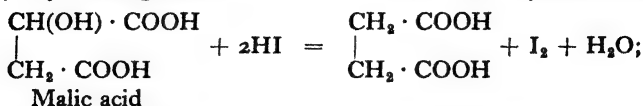
Formation.

1. By the distillation of amber.
2. By the hydrolysis of ethylene cyanide. This method is important, as it affords a synthesis of the acid and a means of determining its constitution:

$$\underset{\text{Ethylene}}{\overset{\text{(Br)}}{\underset{CH_2}{\overset{CH_2}{\|}}}} \longrightarrow \underset{\substack{\text{Ethylene} \\ \text{dibromide}}}{\overset{\text{(KCN)}}{\underset{CH_2Br}{\overset{CH_2Br}{|}}}} \longrightarrow \underset{\substack{\text{Ethylene} \\ \text{cyanide}}}{\overset{\text{(HOH)}}{\underset{CH_2 \cdot CN}{\overset{CH_2 \cdot CN}{|}}}} \longrightarrow \underset{\substack{\text{Succinic} \\ \text{acid}}}{\underset{CH_2 \cdot COOH}{\overset{CH_2 \cdot COOH}{|}}}$$

3. By the reduction of fumaric and maleic acids:

$$\begin{array}{l} CH \cdot COOH \\ \| \\ CH \cdot COOH \end{array} + 2H = \begin{array}{l} CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH \end{array}$$

4. By heating malic acid or tartaric acid with hydriodic acid:

$$\begin{matrix} CH(OH) \cdot COOH \\ | \\ CH_2 \cdot COOH \end{matrix} + 2HI = \begin{matrix} CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH \end{matrix} + I_2 + H_2O;$$

Malic acid

$$\begin{matrix} CH(OH) \cdot COOH \\ | \\ CH(OH) \cdot COOH \end{matrix} + 4HI = \begin{matrix} CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH \end{matrix} + 2I_2 + 2H_2O.$$

Tartaric acid

Properties.—A white crystalline solid, m. pt. 185° C., b. pt. 235° C. It is readily soluble in water. When heated it is converted into an *inner anhydride* or closed-chain compound:

$$\begin{matrix} CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH \end{matrix} = \begin{matrix} CH_2 \cdot CO \\ | \diagdown \\ CH_2 \cdot CO \diagup \end{matrix} O + H_2O$$

Succinic
anhydride
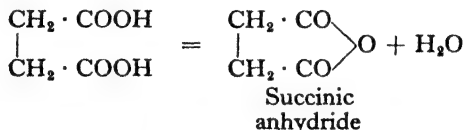
It forms salts known as *succinates*. The ammonium salt decomposes on heating, first into an amide and then into an imide:

$$\begin{matrix} CH_2 \cdot CO \cdot ONH_4 \\ | \\ CH_2 \cdot CO \cdot ONH_4 \end{matrix} \rightarrow \begin{matrix} CH_2 \cdot CO \cdot NH_2 \\ | \\ CH_2 \cdot CO \cdot NH_2 \end{matrix} \rightarrow \begin{matrix} CH_2 \cdot CO \\ | \diagdown \\ CH_2 \cdot CO \diagup \end{matrix} NH$$

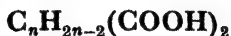Ammonium   Succinamide   Succinimide
succinate
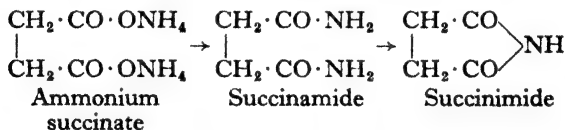
The potassium salt on electrolysis yields ethylene.

Tests for Succinic Acid and Succinates are given on p. 549.

B. UNSATURATED DIBASIC ACIDS
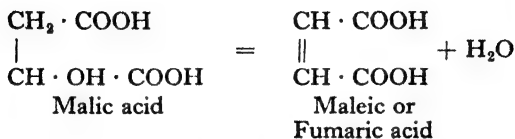
These acids have the general formula

$$C_nH_{2n-2}(COOH)_2$$

and may be regarded as dicarboxylic acids of the olefines. Examples include

Maleic acid ⎫
Fumaric acid ⎭ $C_2H_2(COOH)_2$, from ethylene, C_2H_4.

Maleic Acid and Fumaric Acid,
$$\begin{array}{l} \text{CH} \cdot \text{COOH} \\ \| \\ \text{CH} \cdot \text{COOH.} \end{array}$$

Formation.

1. By dehydrating the hydroxy-dibasic acids, e.g. malic acid:

$$\begin{array}{ccc} \text{CH}_2 \cdot \text{COOH} & & \text{CH} \cdot \text{COOH} \\ | & = & \| & + \text{H}_2\text{O} \\ \text{CH} \cdot \text{OH} \cdot \text{COOH} & & \text{CH} \cdot \text{COOH} \\ \text{Malic acid} & & \text{Maleic or} \\ & & \text{Fumaric acid} \end{array}$$
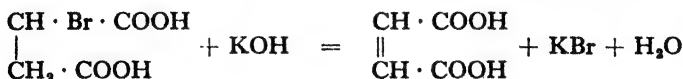
If malic acid is distilled, water and maleic anhydride distil over, leaving behind fumaric acid, the isomer of maleic acid. It will be observed that both maleic acid and fumaric acid are formed at the same time. If the distillation is carried out at about 145° C., however, the chief product is fumaric acid, whereas if the temperature is raised rapidly to 185° C. maleic anhydride is the principal product.

2. *Synthetic Process.*

(*a*) From acetylene di-iodide:

$$\begin{array}{ccccccc} & (\text{I}_2) & & (\text{KCN}) & & (\text{HOH}) & \\ \text{CH} & & \text{CH} \cdot \text{I} & & \text{CH} \cdot \text{CN} & & \text{CH} \cdot \text{COOH} \\ \| \| \| & \longrightarrow & \| & \longrightarrow & \| & \longrightarrow & \| \\ \text{CH} & & \text{CH} \cdot \text{I} & & \text{CH} \cdot \text{CN} & & \text{CH} \cdot \text{COOH} \\ \text{Acetylene} & & \text{Acetylene} & & \text{Acetylene} & & \text{Maleic or} \\ & & \text{di-iodide} & & \text{dicyanide} & & \text{Fumaric acid} \end{array}$$
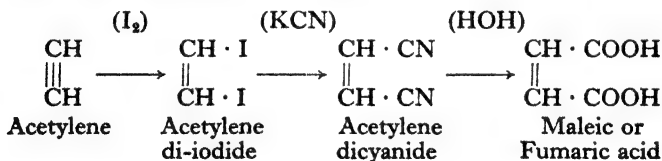
(*b*) From monobromosuccinic acid on treatment with potash or moist silver oxide:

$$\begin{array}{ccc} \text{CH} \cdot \text{Br} \cdot \text{COOH} & & \text{CH} \cdot \text{COOH} \\ | & + \text{KOH} = & \| & + \text{KBr} + \text{H}_2\text{O} \\ \text{CH}_2 \cdot \text{COOH} & & \text{CH} \cdot \text{COOH} \end{array}$$

3. Maleic acid is prepared (*a*) from fumaric acid and phosphorus oxychloride, (*b*) by heating the acetyl derivative of malic acid.

Maleic acid forms colourless large prisms which have a nauseous acid taste. It is soluble in cold water and distils unchanged, although some maleic anhydride is formed at the same time.

Fumaric acid forms colourless small prisms which have a purely acid taste. It is sparingly soluble in cold water and sublimes at about 200° C., forming some maleic anhydride. This acid occurs in Nature in the sap of *Fumaria officinalis*, fungi, Iceland moss, &c.

Isomerism of Maleic and Fumaric Acids

These two acids are isomeric. They are unsaturated acids; they decolorize bromine water and give other reactions characteristic of the double bond.

The configurations of these two acids must be different, and since they do not contain an asymmetric carbon atom their structural representation must differ from that of lactic acid.

Fittig suggested the following formulæ:

$$COOH \cdot CH = CH \cdot COOH \quad \text{and} \quad COOH \cdot CH_2 - \overset{|}{\underset{|}{C}} - COOH$$
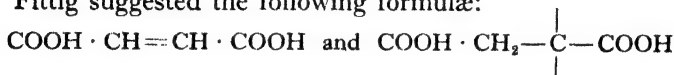
but such isomerism is impossible, since on oxidation both acids yield tartaric acid.

The following formulæ, known as **projection formulæ,** which show a different spatial relationship of the atoms in the molecule, have now been accepted; but in view of the ease with which either acid can be converted into the other, it is more than probable that an enolic isomeride exists, which makes the change easier:
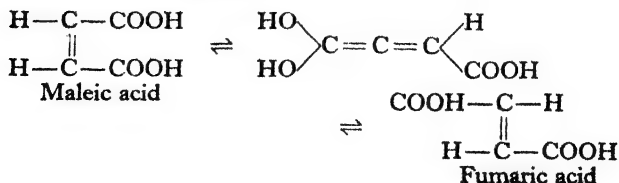
This is an example of the enolization of a carboxyl group, the enolic form containing an oscillatory hydrogen atom.

The tetrahedral arrangement may be represented by a stereo-chemical model representing two tetrahedra united by one of the edges of each.
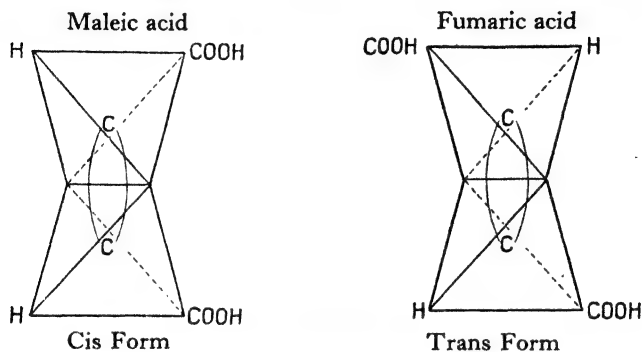

·Fig 33.—Stereo-chemical figures to illustrate Isomers containing a double bond

One of the figures has the two carboxyl groups on the same side and is called the **cis form** (Latin, *cis*, on this side); the other has the two carboxyl groups on opposite sides and is called the **trans form** (Latin, *trans*, across).

Maleic acid is given the cis form since on heating it forms an anhydride, whereas fumaric acid does not.
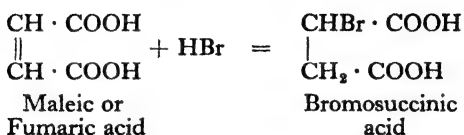
This type of isomerism is known as **ethylene isomerism** or **geometrical isomerism**.

Ethylene or Geometrical Isomerism may be defined as a special type of stereo-isomerism in which the compound contains an ethylenic or double bond and in which the four radicles or groups attached to the doubly linked carbon atoms lie in one plane.

The compound exhibits neither structural asymmetry nor optical activity, and cannot, moreover, be resolved into optically active constituents.

The isomerism of maleic acid and fumaric acid is supported by the following reactions:

1. Both combine with water to form malic acid.

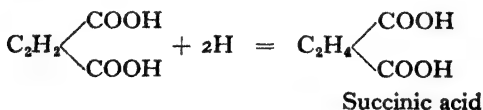2. Both combine with hydrogen bromide to form the same bromosuccinic acid:

$$
\begin{array}{cc}
\begin{array}{l}
\text{CH} \cdot \text{COOH} \\
\parallel \\
\text{CH} \cdot \text{COOH}
\end{array} + \text{HBr} = &
\begin{array}{l}
\text{CHBr} \cdot \text{COOH} \\
\mid \\
\text{CH}_2 \cdot \text{COOH}
\end{array} \\
\begin{array}{c}
\text{Maleic or} \\
\text{Fumaric acid}
\end{array} &
\begin{array}{c}
\text{Bromosuccinic} \\
\text{acid}
\end{array}
\end{array}
$$

3. Both yield stereo-isomeric dibromosuccinic acids with bromine.

4. Both yield stereo-isomeric tartaric acids on careful oxidation:

> Maleic acid forms meso-tartaric acid.
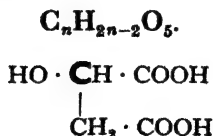>
> Fumaric acid forms racemic acid.

5. Both yield ordinary succinic acid on reduction with either zinc or sodium amalgam:

$$
\text{C}_2\text{H}_2 \Big\langle \begin{array}{l} \text{COOH} \\ \text{COOH} \end{array} + 2\text{H} = \text{C}_2\text{H}_4 \Big\langle \begin{array}{l} \text{COOH} \\ \text{COOH} \end{array}
$$
$$
\text{Succinic acid}
$$

C. Hydroxy-dicarboxylic Acids

Two types are represented by

(a) **Malic acid** or **hydroxy-succinic acid**: general formula

$$
\text{C}_n\text{H}_{2n-2}\text{O}_5.
$$

$$
\begin{array}{l}
\text{HO} \cdot \text{CH} \cdot \text{COOH} \\
\mid \\
\text{CH}_2 \cdot \text{COOH}
\end{array}
$$

(*b*) **Tartaric acid** or **dihydroxy-succinic acid:** general formula

$$C_nH_{2n-2}O_6.$$

$$HO \cdot CH \cdot COOH$$
$$|$$
$$HO \cdot CH \cdot COOH$$
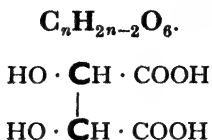
Malic Acid, Hydroxy-succinic Acid,
$$CH \cdot OH \cdot COOH$$
$$|$$
$$CH_2 \cdot COOH$$

Malic acid occurs in unripe apples, grapes, cherries, quinces, &c. (The name malic comes from the Latin *malum*, apple.) It exhibits stereo-isomerism, since it contains an asymmetric carbon atom. All three forms are known.

Formation of (I) inactive malic acid.

1. By the action of moist silver oxide on chloro- or bromo-succinic acid:

$$CH \cdot Cl \cdot COOH$$
$$| \qquad\qquad + AgOH \; = \; $$
$$CH_2 \cdot COOH$$
Chloro-succinic acid

$$CH \cdot OH \cdot COOH$$
$$| \qquad\qquad + AgCl$$
$$CH_2 \cdot COOH$$
Malic acid
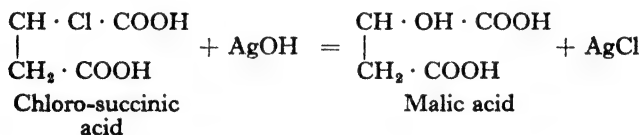
2. By heating maleic or fumaric acid with water in a sealed tube:

$$CH \cdot COOH$$
$$\| \qquad\qquad + HOH \; = \;$$
$$CH \cdot COOH$$

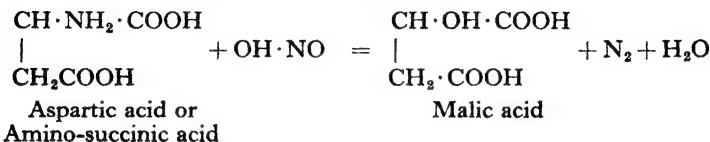$$CH \cdot OH \cdot COOH$$
$$|$$
$$CH_2 \cdot COOH$$
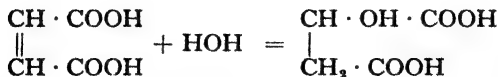
Formation of (II) active malic acid: (a) Lævo-malic acid.

3. From the sap of the sugar maple and the juice of the mountain ash by treatment with milk of lime and oxalic

acid.   Soluble calcium acid malate is formed, which is decomposed by the requisite quantity of oxalic acid.   The calcium is precipitated as calcium oxalate, which is filtered off, and the filtrate is evaporated on the water bath.

4. By the action of nitrous acid on aspartic acid:

$$CH \cdot NH_2 \cdot COOH \atop | \atop CH_2COOH + OH \cdot NO = CH \cdot OH \cdot COOH \atop | \atop CH_2 \cdot COOH + N_2 + H_2O$$

Aspartic acid or   Malic acid
Amino-succinic acid

(*b*) *Dextro-malic acid.*

5. By the **Walden Inversion Method.**

The Walden Inversion may be defined as the conversion of a lævo- or dextro-compound into its mirror image by double substitution.   The inversion is an exception to the general rule that when substitution takes place the group introduced into the molecule takes the place of the radicle removed, that is, the structure is not changed.

Substitution may be (*a*) *direct*: in this case, commencing with lævo-chlorosuccinic acid, we may replace the chlorine by an —OH group.   If the chloro-acid is hydrolysed with moist silver oxide, the resulting product is lævo-malic acid. This substitution is unaccompanied by any displacement of the other three radicles of the asymmetric carbon atom.

(*b*) *Indirect*: in this case, commencing with lævo-malic acid, we may replace the —OH group by a chlorine atom on treatment with phosphorus pentachloride; then dextro-chlorosuccinic acid is formed.   If this chloro-acid is hydrolysed with *moist silver oxide*, dextro-malic acid, the mirror image of the lævo-acid, is obtained.   If the chloro-acid, however, is hydrolysed with *potassium hydroxide* the lævo-acid is re-formed.

These reactions were discovered by Walden.

The complete cycle for the inversion of malic acid may be represented as follows:

$$HO \cdot CH \cdot COOH$$
$$|$$
$$CH_2 \cdot COOH$$

l-malic acid

Ag$_2$O

PCl$_5$

KOH

l-chlorosuccinic acid

d-chlorosuccinic acid

PCl$_5$

$$CH \cdot OH \cdot COOH$$
$$|$$
$$CH_2 \cdot COOH$$

KOH

Ag$_2$O
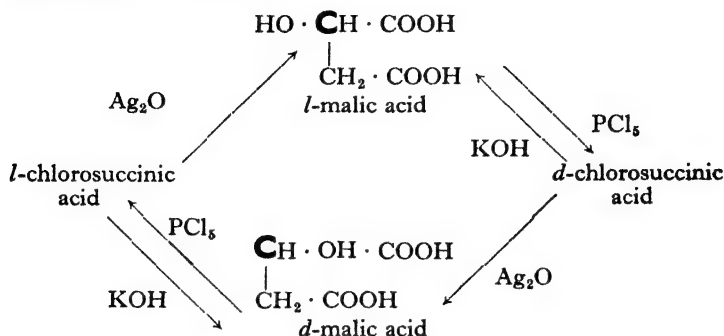
d-malic acid

l-chloro-acid → *l*-malic acid → *d*-chloro-acid → *d*-malic acid
Cl—CH— → OH—CH— → CH—Cl— → CH—OH—

The Walden Inversion applies to other compounds which contain an asymmetric carbon atom attached to a carboxyl group.

Properties of Malic Acid.—Colourless hygroscopic needles, m. pt. 100° C. It is readily soluble in water and alcohol, but sparingly soluble in ether. On distillation maleic anhydride distils over, leaving fumaric acid as the residue. The natural acid is lævo-rotatory in dilute solutions, but when the concentration increases to over 35 per cent, the acid becomes dextro-rotatory. A 35 per cent solution is optically inactive at 20° C.

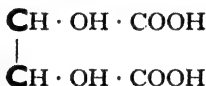When boiled with hydriodic acid, malic acids are reduced to succinic acid (p. 292).

When treated with hydrobromic acid, they are converted into monobromosuccinic acid:

$$CH \cdot OH \cdot COOH$$
$$| \qquad\qquad + HBr = $$
$$CH_2 \cdot COOH$$

$$CH \cdot Br \cdot COOH$$
$$| \qquad\qquad + HOH$$
$$CH_2 \cdot COOH$$

Monobromosuccinic acid
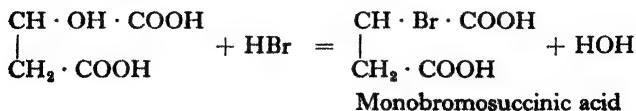
When oxidized, malic acids yield oxalo-acetic acid; this shows the presence of a secondary alcohol group (—CH·OH):

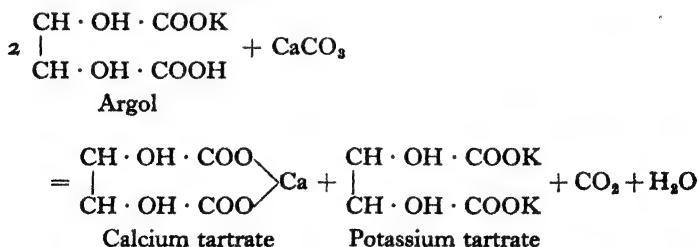$$\begin{array}{l} \text{CH} \cdot \text{OH} \cdot \text{COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array} + \text{O} = \begin{array}{l} \text{CO} \cdot \text{COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array} + \text{HOH}$$
Oxalo-acetic acid
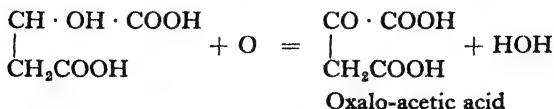
Tartaric Acid, Dihydroxy-succinic Acid,

$$\begin{array}{l} \mathbf{C}\text{H} \cdot \text{OH} \cdot \text{COOH} \\ | \\ \mathbf{C}\text{H} \cdot \text{OH} \cdot \text{COOH} \end{array}$$

Occurrence.—In sour grapes, in berries of mountain ash, and in other fruits, and as " Argol " in the fermentation of grape sugar.
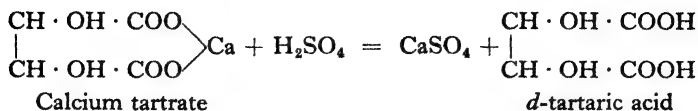
Formation.

1. *Industrially*, from " Argol " (potassium hydrogen tartrate). Argol is first recrystallized from hot water and the product is then boiled with limestone; calcium tartrate is precipitated, leaving normal potassium tartrate in solution:

$$2 \begin{array}{l} \text{CH} \cdot \text{OH} \cdot \text{COOK} \\ | \\ \text{CH} \cdot \text{OH} \cdot \text{COOH} \end{array} + \text{CaCO}_3$$
Argol

$$= \begin{array}{l} \text{CH} \cdot \text{OH} \cdot \text{COO} \\ | \\ \text{CH} \cdot \text{OH} \cdot \text{COO} \end{array}\!\!\!\!>\!\text{Ca} + \begin{array}{l} \text{CH} \cdot \text{OH} \cdot \text{COOK} \\ | \\ \text{CH} \cdot \text{OH} \cdot \text{COOK} \end{array} + \text{CO}_2 + \text{H}_2\text{O}$$
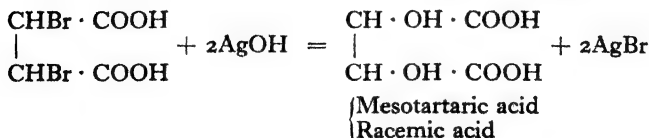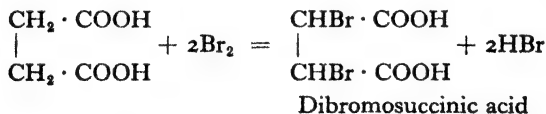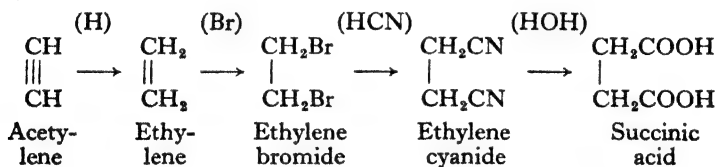Calcium tartrate   Potassium tartrate

The soluble potassium tartrate is then precipitated as calcium tartrate by the addition of the requisite quantity of calcium chloride. The calcium tartrate is separated, washed with water and decomposed with the theoretical amount of sulphuric acid. The solution is filtered off from

the precipitated calcium sulphate and finally evaporated until crystallization takes place.

$$\left.\begin{array}{l} CH \cdot OH \cdot COO \\ | \\ CH \cdot OH \cdot COO \end{array}\right\rangle Ca + H_2SO_4 = CaSO_4 + \begin{array}{l} CH \cdot OH \cdot COOH \\ | \\ CH \cdot OH \cdot COOH \end{array}$$

Calcium tartrate d-tartaric acid

Tartaric acid obtained from natural products is dextro-rotatory.

2. *Synthetically*, from succinic acid.   Succinic acid is prepared as outlined below, and is then converted into dibromosuccinic acid by heating it with bromine and amorphous phosphorus. The dibromo-derivative is treated with moist silver oxide; insoluble silver bromide is formed and filtered off. The filtrate is then evaporated; the inactive acid crystallizes out. The inactive acid consists mainly of mesotartaric acid together with racemic acid (see below, p. 305).

$$\underset{\substack{\text{Acety-}\\\text{lene}}}{\overset{\text{(H)}}{\underset{CH}{\overset{CH}{|||}}}} \longrightarrow \underset{\substack{\text{Ethy-}\\\text{lene}}}{\overset{\text{(Br)}}{\underset{CH_2}{\overset{CH_2}{||}}}} \longrightarrow \underset{\substack{\text{Ethylene}\\\text{bromide}}}{\overset{\text{(HCN)}}{\underset{CH_2Br}{\overset{CH_2Br}{|}}}} \longrightarrow \underset{\substack{\text{Ethylene}\\\text{cyanide}}}{\overset{\text{(HOH)}}{\underset{CH_2CN}{\overset{CH_2CN}{|}}}} \longrightarrow \underset{\substack{\text{Succinic}\\\text{acid}}}{\underset{CH_2COOH}{\overset{CH_2COOH}{|}}}$$

$$\begin{array}{l} CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH \end{array} + 2Br_2 = \begin{array}{l} CHBr \cdot COOH \\ | \\ CHBr \cdot COOH \end{array} + 2HBr$$

Dibromosuccinic acid

$$\begin{array}{l} CHBr \cdot COOH \\ | \\ CHBr \cdot COOH \end{array} + 2AgOH = \begin{array}{l} CH \cdot OH \cdot COOH \\ | \\ CH \cdot OH \cdot COOH \end{array} + 2AgBr$$

$\left\{\begin{array}{l}\text{Mesotartaric acid}\\\text{Racemic acid}\end{array}\right.$

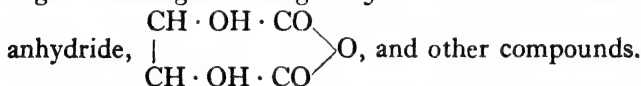Tartaric acid obtained synthetically is optically inactive.

3. From glyoxal.   This compound combines directly

with hydrogen cyanide to form dicyanhydrin, which is hydrolysed by mineral acids, forming racemic acid.

$$
\begin{array}{c}
\text{CHO} \\
| \\
\text{CHO}
\end{array}
+ 2\text{HCN} =
\begin{array}{c}
\text{CH(OH)} \cdot \text{CN} \\
| \\
\text{CH(OH)} \cdot \text{CN}
\end{array}
$$

Glyoxal   Dicyanhydrin

$$
\begin{array}{c}
\text{CH} \cdot \text{OH} \cdot \text{CN} \\
| \\
\text{CH} \cdot \text{OH} \cdot \text{CN}
\end{array}
+ 4\text{HOH} =
\begin{array}{c}
\text{CH} \cdot \text{OH} \cdot \text{COOH} \\
| \\
\text{CH} \cdot \text{OH} \cdot \text{COOH}
\end{array}
+ 2\text{NH}_3
$$
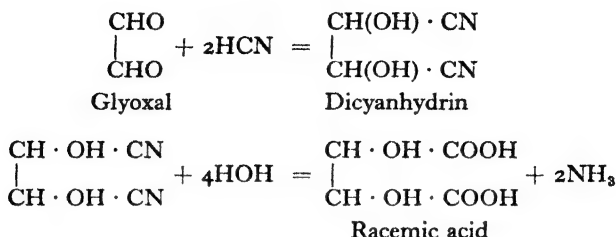
Racemic acid

4. The lævo-acid is obtained by resolving racemic acid (p. 307).

Properties.—Large transparent crystals, readily soluble in water and in alcohol but insoluble in ether, m. pt. 170° C. When heated strongly, tartaric acid emits an odour of burnt sugar. Prolonged heating at 150° C. converts it into tartaric anhydride,
$$
\begin{array}{c}
\text{CH} \cdot \text{OH} \cdot \text{CO} \\
| \\
\text{CH} \cdot \text{OH} \cdot \text{CO}
\end{array}\hspace{-4pt}\Big\rangle\text{O},
$$
and other compounds.

On dry distillation tartaric acid yields pyruvic acid, pyrotartaric acid and other products. It is a dibasic acid, forming both normal and acid tartrates, some of which are important. Tartaric acid is very reactive and can form a large number of alkyl, acyl, and alkylidene derivatives.

Uses.—In medicine, in dyeing; in the manufacture of certain baking powders, and "sherbet" and other effervescing drinks. Its use in chemical analysis depends on its property of preventing the precipitation of certain metallic hydroxides by alkalis.

Tartrates.

Acid Potassium Tartrate, Potassium Hydrogen Tartrate, Cream of Tartar:

$$
\begin{array}{c}
\text{CH} \cdot \text{OH} \cdot \text{COOK} \\
| \\
\text{CH} \cdot \text{OH} \cdot \text{COOH}
\end{array}
$$
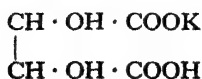
Formation.

1. By adding excess of tartaric acid to a concentrated solution of the normal salt; acid potassium tartrate is precipitated, as it is only sparingly soluble.

2. By adding the equivalent amount of mineral acid to the normal salt:

$$
\begin{array}{l} CH \cdot OH \cdot COOK \\ | \\ CH \cdot OH \cdot COOK \end{array} + HCl = \begin{array}{l} CH \cdot OH \cdot COOK \\ | \\ CH \cdot OH \cdot COOH \end{array} + KCl
$$
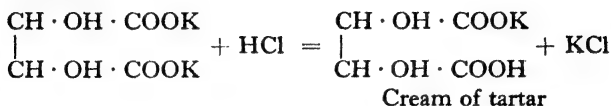
Cream of tartar

It is known in commerce as *Argol*. The impure salt has a reddish colour. The purified salt is colourless and is known as *Cream of Tartar*; it is used in medicine and in baking powders. Cream of Tartar baking powders are mixtures of the acid salt and sodium bicarbonate with flour or starch. With water these compounds interact as follows:

$$
\begin{array}{l} CH \cdot OH \cdot COOK \\ | \\ CH \cdot OH \cdot COOH \end{array} + NaHCO_3 = \begin{array}{l} CH \cdot OH \cdot COOK \\ | \\ CH \cdot OH \cdot COONa \end{array} + CO_2 + H_2O
$$

Cream of tartar   Rochelle salt
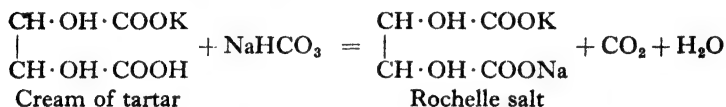
The carbon dioxide which is liberated raises the dough.

Normal Potassium Tartrate,

$$
2 \begin{array}{l} CH \cdot OH \cdot COOK \\ | \\ CH \cdot OH \cdot COOK \end{array} \cdot H_2O.
$$
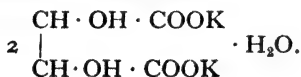
This is obtained by neutralizing the acid or the acid salt with potassium hydroxide. It is readily soluble in water.

Potassium Sodium Tartrate, Rochelle Salt,

$$
\begin{array}{l} CH \cdot OH \cdot COOK \\ | \\ CH \cdot OH \cdot COONa \end{array} \cdot 4H_2O,
$$
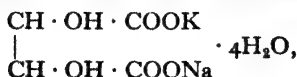
is formed by neutralizing the acid salt with sodium carbonate. It is obtained as large transparent crystals, which are

used in the preparation of Fehling's solution (p. 527) and of Seidlitz powder. It is used as a laxative. It takes its name from Seignette of La Rochelle, who discovered it.

Seidlitz Powder consists of:

1. Tartaric acid in the white paper.
2. A mixture of Rochelle salt and sodium bicarbonate in the blue paper.

These are dissolved separately; when the solutions are mixed the carbon dioxide liberated makes the dose pleasanter to take.
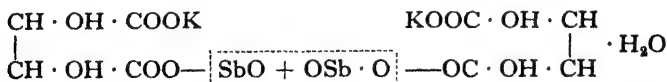
Tartar Emetic, Potassium Antimonyl Tartrate,

$$\begin{matrix} CH \cdot OH \cdot COOK \\ | \\ CH \cdot OH \cdot COO \cdot SbO \end{matrix} \cdot \tfrac{1}{2}H_2O,$$
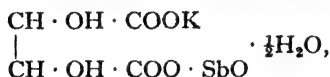
is obtained by boiling acid potassium tartrate with antimonious oxide and water:

$$2KHC_4H_4O_6 + Sb_2O_3 = 2K(SbO)C_4H_4O_6 + H_2O$$
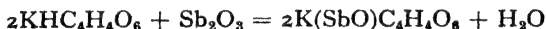
Two molecules of this salt contain one molecule of antimonious oxide:

$$\begin{matrix} CH \cdot OH \cdot COOK & & KOOC \cdot OH \cdot CH \\ | & & | \\ CH \cdot OH \cdot COO - \overline{SbO + OSb \cdot O} - OC \cdot OH \cdot CH \end{matrix} \cdot H_2O$$

The crystals obtained are soluble in water and are used in medicine as an emetic, and in dyeing as a mordant.

Calcium Tartrate occurs in grapes and in senna leaves. Its formula is:

$$\begin{matrix} CH \cdot OH \cdot COO \\ | \qquad\qquad\quad \diagdown \\ \qquad\qquad\qquad Ca \cdot 4H_2O \\ | \qquad\qquad\quad \diagup \\ CH \cdot OH \cdot COO \end{matrix}$$
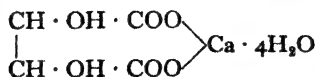
It is formed by precipitation on adding a soluble calcium

salt to a neutral solution of a tartrate. It is soluble in potash, but is reprecipitated on boiling the solution.

Tests for Tartaric Acid and Tartrates are given on p. 546.

Isomerism of the Tartaric Acids

Tartaric acid contains two asymmetric carbon atoms, and four isomeric acids are known, all of which have this structural formula:

$$\begin{array}{ll} \mathbf{C} \cdot \mathrm{H} \cdot \mathrm{OH} \cdot \mathrm{COOH} & \\ | & \text{or} \\ \mathbf{C} \cdot \mathrm{H} \cdot \mathrm{OH} \cdot \mathrm{COOH} & \end{array} \qquad \begin{array}{l} \mathrm{HO} \diagdown \quad /\mathrm{H} \\ \qquad \mathbf{C} \diagdown\!\!\!—\mathrm{COOH} \\ \qquad | \\ \qquad \mathbf{C}\!—\!\mathrm{COOH} \\ \mathrm{HO} \diagup \quad \diagdown \mathrm{H} \end{array}$$
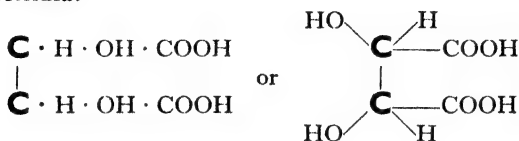
These acids are distinguished as

1. Dextro- or *d*-tartaric acid (m. pt. 170° C.).
2. Lævo- or *l*-tartaric acid (m. pt. 170° C.).

·3. Racemic acid (m. pt. 206° C.); optically inactive and consists of equal parts of the dextro- and lævo-acids.

4. Meso-tartaric acid (m. pt. 143° C.); optically inactive and cannot be resolved into active acids.

From the above formula, there are three possible arrangements in space of the groups attached to the asymmetric carbon atoms. These may be illustrated by a stereo-chemical model consisting of two tetrahedrons united by one apex of each (fig. 34). The two-dimensional formulæ are also given (fig. 34, p. 306).

Models I and II contain *no* plane of symmetry and are related to one another as object and image. They thus represent the two optically active acids.

Model III has *one* plane of symmetry and is optically inactive, for if the upper half is dextro-rotatory, the lower half is lævo-rotatory to an equal and opposite amount.

Model III is therefore taken to represent meso-tartaric acid. Its inactivity is attributed to **Internal Compensation,**

one tetrahedron (i.e. one half of the molecule) neutralizing the effect of the other.

Racemic acid is inactive and is a combination of equal amounts of Models I and II. Its inactivity is attributed to
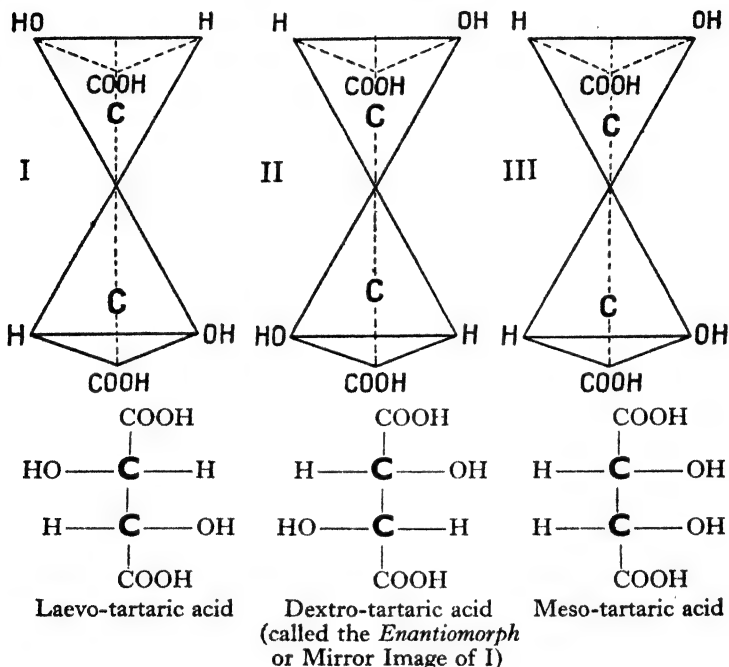
Fig. 34.—Absolute configurations of laevo-, dextro-, and meso-tartaric acids

External Compensation, the rotations of the dextro- and lævo-constituents neutralizing one another.

The term **racemic** has now been extended to any compounds and mixtures which are optically inactive because they contain equal amounts of a dextro- and a lævo-constituent. Racemic compounds may be resolved into their optically active constituents by several methods, most of which were devised by Pasteur.

Resolution of Racemic Acid.

Method 1.—By mechanical separation. When sodium ammonium racemate is allowed to crystallize from water, rhombic crystals are obtained having the composition

$$Na \cdot NH_4 \cdot C_4H_4O_6 \cdot 2H_2O$$

(a) Dextro-rotatory   (b) Lævo-rotatory   (c) Inactive
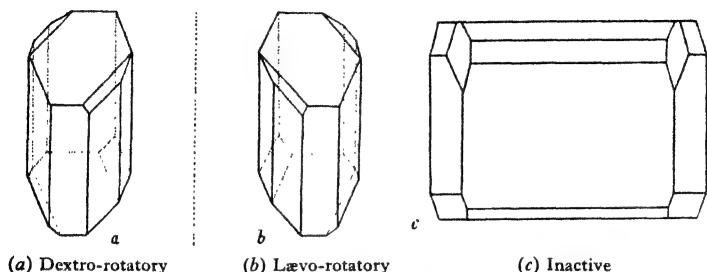
Fig. 35.—(a), (b) Hemihedral Crystals of Sodium Ammonium Tartrate (Pasteur).
(c) Holohedral Crystal of Sodium Ammonium Tartrate (Scacchi)

These crystals are of two kinds, one of which is the mirror image of the other (fig. 35).

If these crystals are mechanically separated and the free acid is liberated from each kind, one acid is found to be dextro-rotatory and the other lævo-rotatory. When quantities of the concentrated solutions of the two acids are mixed, heat is liberated and inactive racemic acid is formed.

(a) Dextro-rotatory   (b) Lævo-rotatory   (c) Inactive
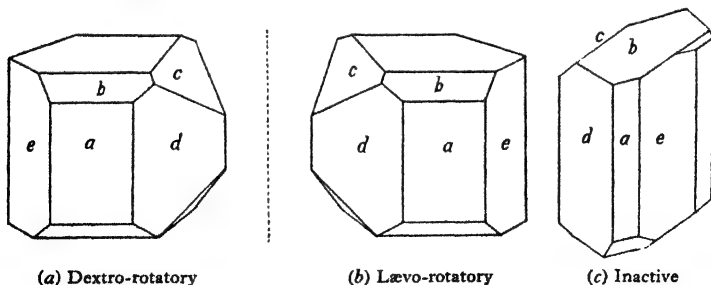
Fig. 36.—(a), (b) Hemihedral Crystals of Tartaric Acid (Pasteur).
(c) Holohedral Crystal of Racemic Tartaric Acid

Method 2.—By combination with an optically active base. Pasteur used *l*-cinchonine. This base combines with both the dextro- and the lævo-acid to form salts which are not mirror images of one another; these can be separated by fractional crystallization, as their solubilities are different. The acids can then be recovered separately from these salts.

Method 3.—Biochemical method: by the action of the green mould *Penicillium glaucum* (or *Aspergillus niger*, &c.). This mould when allowed to develop in ammonium racemate destroys the salt of the dextro-tartaric acid and leaves the ammonium salt of lævo-tartaric acid in solution. The lævo-acid can then be obtained by ordinary methods.

Racemization.

When one group replaces another, the carbon atom remaining asymmetric, the product is not always optically active. This is due to racemization, i.e. the conversion of one-half of the active substance into its optical isomer. That the loss of optical activity is due to this rather than to the formation of some structurally different inactive compound is shown by the fact that the product can be resolved into its active constituents. Racemization is usually effected by rise of temperature. Thus active lactic acid and active amyl alcohol are rendered inactive by strong heating. Heating with 10 to 15 per cent of water in sealed tubes at 175° C. for several hours racemizes active mandelic acid $[C_6H_5CH(OH) \cdot COOH]$, tartaric acid, aspartic acid, and other acids.

The presence of foreign substances often causes racemization; e.g. boiling with potassium hydroxide solution racemizes active amyl alcohol, lactic and mandelic acids, and *d*-valeric acid loses its activity on being heated with concentrated sulphuric acid.

Racemization seems to occur more readily when substances are in process of formation than when they are
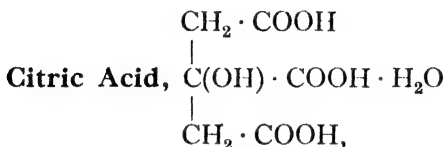
already formed; hence the change takes place during chemical reactions, that is, the replacement of one group by another. For example, active malic acid treated with phosphorus pentabromide is converted into inactive bromosuccinic acid.

D. Mono-hydroxy Tribasic Acids

These have the general formula

$$C_nH_{2n-4}O_7.$$
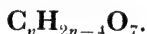
Citric acid is the chief representative of this class.

$$\text{Citric Acid,} \quad \begin{array}{c} CH_2 \cdot COOH \\ | \\ C(OH) \cdot COOH \cdot H_2O \\ | \\ CH_2 \cdot COOH, \end{array}$$

occurs in orange and lemon juice, in gooseberries, raspberries, and other berries and fruits.

Formation.

1. *Industrially* (*a*) From the juice of lemons. Lemon juice, which contains about 6 per cent of the free acid, is first concentrated until the acid content rises to 60 per cent. Chalk is then added to neutralize the acid and the solution is boiled; insoluble calcium citrate is deposited. This salt is filtered off whilst hot, and decomposed with the requisite amount of sulphuric acid; the calcium sulphate is filtered off and the filtrate evaporated. On cooling crystals of citric acid separate.

$$\underset{\text{Calcium citrate}}{(C_6H_5O_7)_2Ca_3} + 3H_2SO_4 = 3CaSO_4 + \underset{\text{Citric acid}}{2C_6H_8O_7}$$
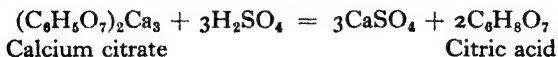
Note.—Calcium citrate is fairly soluble in cold water, but only sparingly soluble in hot water.

(*b*) By the fermentation of glucose with special moulds, such as *Citromycetes pfefferianus* and *Citromycetes glaber*:

$$2C_6H_{12}O_6 + 15O = C_6H_8O_7 + 6CO_2 + 8H_2O$$

Glucose   Citric acid

2. *Synthetically* from glycerol as follows:

$$\left(\begin{matrix}HCl\\gas\end{matrix}\right) \qquad (O) \qquad\quad (HCN) \qquad\quad (HOH)$$

```
 CH₂OH        CH₂Cl         CH₂Cl        CH₂Cl
  |            |             |            |
 CH·OH   ⟶    CH·OH   ⟶     CO     ⟶     C(OH)·CN  ⟶
  |            |             |            |
 CH₂OH        CH₂Cl         CH₂Cl        CH₂Cl
 Glycerol   Dichlorhydrin   1 : 3-dichlor-  Dichloracetone
                             acetone        cyanhydrin
```

```
          (HCN)              (HOH)
 CH₂Cl              CH₂CN              CH₂·COOH
  |                 |                  |
⟶ C(OH)·COOH   ⟶   C(OH)·COOH   ⟶    C(OH)·COOH
  |                 |                  |
 CH₂Cl             CH₂CN              CH₂·COOH
  Dichlor-α-        Dicyan-α-          Citric acid
hydroxybutyric acid  hydroxybutyric acid
```
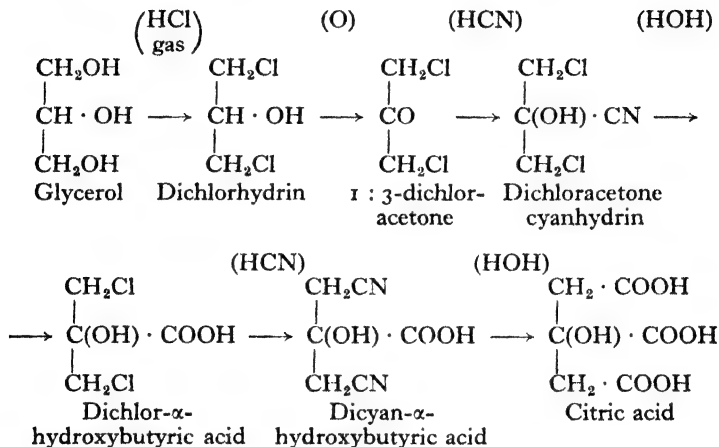
Properties.—Citric acid is a white crystalline substance containing one molecule of water of crystallization (m. pt. 153° C.). It loses its water of crystallization above 100° C. When heated rapidly it chars but gives off no odour of burnt sugar. When heated to 180° C., it forms an unsaturated tribasic acid, aconitic acid:

```
 CH₂·COOH          CH·COOH
  |                 ‖
 C(OH)·COOH   =     C·COOH    + HOH
  |                 |
 CH₂·COOH          CH₂·COOH
  Citric acid        Aconitic acid
```
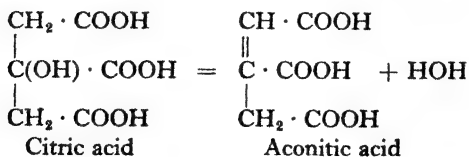
It is a tricarboxylic acid containing one hydroxyl group, and is therefore tribasic. It contains no asymmetric carbon

atom and therefore does not exhibit optical activity. It is very soluble in water, less soluble in alcohol, and sparingly soluble in ether. Like many hydroxy acids (e.g. tartaric), it prevents the precipitation of certain metallic hydroxides (e.g. copper, iron, zinc) by alkalis. It forms salts known as *citrates*.

The presence of the hydroxyl group is shown by the action of acetyl chloride on the ethyl ester of citric acid; an acetyl derivative is obtained:

<div align="center">

(C_2H_5OH) (CH_3COCl)

</div>

$$
\begin{array}{ccc}
CH_2COOH & CH_2COOC_2H_5 & CH_2COOC_2H_5 \\
| & | & | \quad COOCH_3 \\
C(OH){\cdot}COOH \longrightarrow & C(OH)COOC_2H_5 \longrightarrow & C\!\!< \\
| & | & | \quad COOC_2H_5 \\
CH_2COOH & CH_2COOC_2H_5 & CH_2COOC_2H_5 \\
\text{Citric acid} & \text{Triethyl citrate} & \text{Acetyl triethyl} \\
& & \text{citrate}
\end{array}
$$
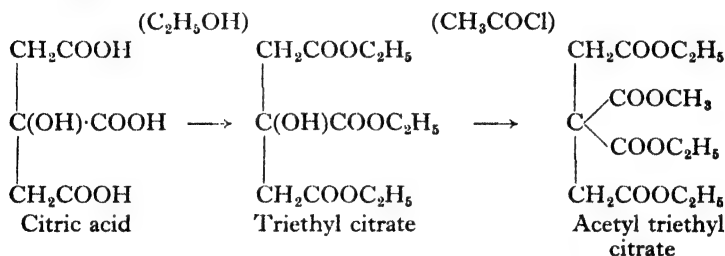
Uses.—Citric acid is used in the manufacture of lemon and other drinks, and in calico-printing. In the form of ferric ammonium citrate it is used in the manufacture of blue-print paper.

The free acid is used as a preventative of scurvy, and the citrates of iron, ammonium, bismuth and magnesium have medicinal properties. Magnesium citrate is used as a laxative.

Tests for Citric Acid and Citrates are given on p. 547.

<div align="center">

QUESTIONS

</div>

1. Suggest a method for preparing (*a*) acetylene from ethyl alcohol, (*b*) methane from acetic acid, (*c*) carbon monoxide from oxalic acid.

If two litres of acetylene were mixed with six litres of oxygen and exploded, what would be the volume and composition of the gaseous product if measured at 720 mm. and 100° C.? (*Prel. Sc.*)

2. What reactions occur when oxalic acid is heated with (*a*) sulphuric acid, (*b*) glycerol?

Describe how you would isolate specimens of the products of the reactions.   (*Cambridge Higher School Cert.*)

3. How is ethyl alcohol prepared on the industrial scale? Give details for the conversion of this substance into (*a*) diethyl ether, (*b*) ethane, (*c*) ethyl oxalate.

(*London Higher School Cert.*)

4. Outline the steps by means of which *three* of the following conversions may be effected:

        (*a*) Ethyl alcohol to ethyl acetate.
        (*b*) Acetic acid to acetamide.
        (*c*) Oxalic acid to formic acid.
        (*d*) Methyl alcohol to formaldehyde.
(*Cambridge Higher School Cert.*)

5. How would you ascertain the presence or absence in an organic compound of the following groups: (*a*) hydroxyl, (*b*) carbonyl, (*c*) a nitro-group, (*d*) methoxyl, (*e*) sulphoxyl, (*f*) an ethylenic linkage? Indicate briefly how you would estimate any one of these quantitatively.

6. Describe the preparation of tartaric acid and explain the reactions by which it may be identified. Write its constitutional formula and state briefly how it may be prepared synthetically.
(*Chemists and Druggists Qual.*)

7. How does oxalic acid differ in physical and chemical properties from acetic acid?

What is the effect of (*a*) treating iron rust with oxalic acid, (*b*) heating oxalic acid, (*c*) heating oxalic acid with concentrated sulphuric acid, (*d*) treating oxalic acid with caustic soda?

8. Starting with ethylene, indicate briefly how *two* of the following may be synthesized: succinic acid, tartaric acid, oxalic acid, ethyl alcohol.

9. What is meant by isomerism? Write the structural formulæ of *two* isomers containing chlorine, of *two* containing nitrogen,

and of *two* isomeric esters. Describe *one* chemical method of distinguishing between each pair of isomers.

Briefly describe the isomerism of the tartaric acids.

(Oxford Higher School Cert.)

10. What is the natural source of tartaric acid? How is the acid prepared from it?

Starting with tartaric acid, how would you prepare " cream of tartar ", and " tartar emetic "?

Explain the existence of two optically active and two optically inactive forms of tartaric acid.

11. What do you understand by isomerism?

Discuss the different types of isomerism, illustrating your answer by reference to (*a*) the butyl alcohols, (*b*) the tartaric acids, (*c*) maleic and fumaric acids, (*d*) allyl alcohol and acetone.

12. How is oxalic acid made on the large scale? What reactions occur between oxalic acid and (*a*) alcohol, (*b*) sulphuric acid, (*c*) phosphorus pentachloride? *(Phar. Chem. Qual.)*

13. Explain with two examples in each case the following terms: (*a*) unsaturated compound, (*b*) racemic mixture, saponification, (*d*) polymerization, (*e*) homologous series.

(Civil Service: Executive Group.)

14. Define exactly (*a*) Isomerism, (*b*) Stereo-isomerism. Illustrate your answer by reference to examples.

15. Write an account of the effect of the position of either:

(*a*) The hydroxyl group in the hydroxy-acids; or, (*b*) the amino-group in the amino-acids, on the chemical properties of the respective group of substances.

16. An organic acid has the molecular formula $C_3H_6O_3$. In what isomeric forms may it exist?

Explain clearly the relationship between the isomerides.

(Cambridge Higher School Cert.)

CHAPTER XII

Urea or Carbamide, $CO(NH_2)_2$

Occurrence.—Urea is a compound of great physiological importance. It occurs in the urine of mammals, of carnivorous birds, of some reptiles and also in other animal fluids. It is formed by the decomposition of the proteins in the system. It is one of the principal nitrogenous components of human urine, of which it forms about 2 to 3 per cent. About 30 gm. are excreted daily by man.

This compound was discovered in urine in 1773, and was first artificially produced by Wöhler (1828), who found that when an aqueous solution of ammonium cyanate is evaporated the salt is converted into urea.

Formation.

1. By the oxidation of an ammoniacal solution of either glucose or formaldehyde. The glucose is first converted into formaldehyde; on further oxidation both ammonium cyanate and urea are formed.

$$C_6H_{12}O_6 \longrightarrow \underset{\substack{\text{Formal-} \\ \text{dehyde}}}{6HCHO}$$

$$HCHO + 2NH_3 + 2O = \underset{\substack{\text{Ammonium} \\ \text{cyanate}}}{NH_4CNO} + 2H_2O$$

$$NH_4CNO = \underset{\text{Urea}}{CO(NH_2)_2}$$
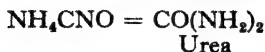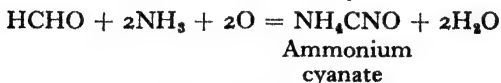
The formation of urea in the animal system is probably based on these reactions.

2. By the action of ammonia on carbonyl chloride (phosgene), ethyl carbonate, and ethyl carbamate:

A. $CO\diagup_{Cl}^{Cl} + {H \cdot NH_2 \atop H \cdot NH_2} + 2NH_3 = CO\diagup_{NH_2}^{NH_2} + 2NH_4Cl$

    Carbonyl   Urea

    chloride

B. $CO\diagup_{OC_2H_5}^{OC_2H_5} + {H \cdot NH_2 \atop H \cdot NH_2} = CO\diagup_{NH_2}^{NH_2} + 2C_2H_5OH$
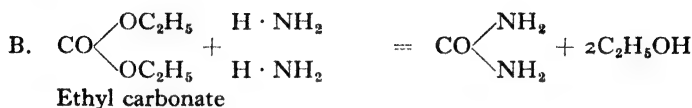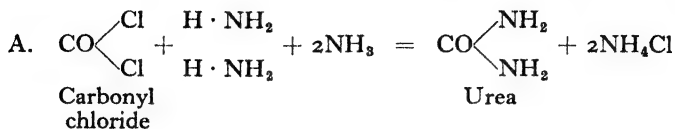
    Ethyl carbonate

In all probability the reaction between ammonia and ethyl carbonate takes places in stages, ethyl carbamate being formed as an intermediate product:

(a) $CO\diagup_{OC_2H_5}^{OC_2H_5} + {H \atop NH_2} = CO\diagup_{OC_2H_5}^{NH_2} + C_2H_5OH$

(b) $CO\diagup_{OC_2H_5}^{NH_2} + {NH_2 \atop H} = CO\diagup_{NH_2}^{NH_2} + C_2H_5OH$

    Ethyl carbamate
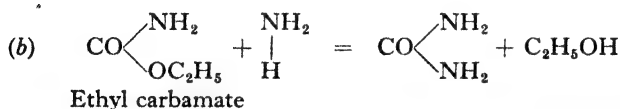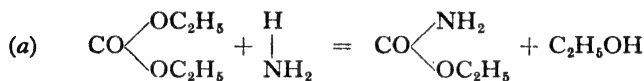
3. Synthetically by the molecular transformation of ammonium cyanate, by warming its aqueous solution or by allowing it to stand; or by heating together a mixture of potassium cyanide and red lead.

Experiment.—Weigh out in a basin 40 gm. of potassium or sodium cyanide and 100 gm. of red lead. Heat gently with stirring until the mixture is just fused. The melt is then poured out on to a cold slab, and the mass is powdered and lixiviated with 200 c.c. of water for an hour to separate impurities. The solution is filtered, and to the filtrate, which contains potassium cyanate, are added 40 gm. of ammonium sulphate dissolved in the smallest possible quantity of water. The mixture is then evaporated with constant stirring on

a water bath to dryness. The residue is broken up and boiled with about 50 c.c. of methylated spirits on a water bath. The alcohol dissolves the urea and the solution is filtered into a crystallizing dish. Long prismatic needles of urea deposit on cooling. The reactions are as follows:

$$4KCN + Pb_3O_4 = 4KCNO + 3Pb,$$
$$2KCNO + (NH_4)_2SO_4 = K_2SO_4 + 2NH_4CNO,$$
$$NH_4-O-C \equiv N \rightleftharpoons NH_2-CO-NH_2.$$
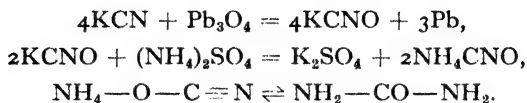
As the latter reaction is reversible the conversion is never complete, but only a very small amount of the cyanate is left when equilibrium is reached.

It will be observed that ammonium cyanate and urea are isomeric but the atoms of the molecules of the two compounds are arranged differently. The conversion of the one into the other is called an **intramolecular** change because it merely involves a rearrangement of the atoms within the molecule.

4. (The usual method). By mixing a solution of potassium cyanate with ammonium sulphate in equimolecular proportions and evaporating the mixture. The ammonium cyanate first formed is converted into urea as explained above, and the urea may be extracted from the dried mass with alcohol, which dissolves the urea but not the potassium sulphate.

5. By abstracting the elements of water from carbonate or carbamate of ammonia. Dry carbon dioxide and ammonia combine together to form ammonium carbamate, the so-called anhydrous carbonate of ammonia, which is transferred into urea when heated to 135° C. or when exposed to an alternating current of electricity:

$$NH_2CO \cdot ONH_4 = CO(NH_2)_2 + H_2O$$

Ammonium   Urea
carbamate
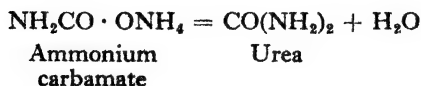
6. By the addition of water to cyanamide:

$$NH_2CN + H_2O = CO(NH_2)_2$$
Cyanamide
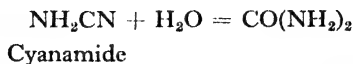
7. By heating a solution of carbon monoxide in ammoniacal cuprous chloride:

$$CO + 2NH_3 + Cu_2Cl_2 = CO(NH_2)_2 + 2HCl + 2Cu$$

8. From urine. Urine is evaporated to a small bulk and concentrated nitric acid is added; urea nitrate is precipitated and then crystallized from nitric acid. It is next dissolved in hot water and decomposed by barium carbonate. The solution is evaporated to dryness and the urea extracted with alcohol, in which barium nitrate is insoluble. The alcoholic solution is filtered off and the urea can then be crystallized from the filtrate.

$$2CO(NH_2)_2 \cdot HNO_3 + BaCO_3 = 2CO(NH_2)_2 + Ba(NO_3)_2 + H_2O + CO_2$$

When urine is exposed to the air and to certain micro-organisms, e.g. *micrococcus ureae*, in the soil, fermentation sets in, the urea being converted into ammonium carbonate:

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3$$

The smell of ammonia in urinals and stables is due to the decomposition of urea or hippuric acid.

Properties.—Urea occurs as large rhombic colourless crystals on crystallization from alcohol (m. pt. 132° C.). It is readily soluble in water and alcohol but insoluble in ether and chloroform. Above 132° C. it begins to decompose; on further heating it decomposes completely; the chief products of decomposition are ammonia, carbon dioxide, biuret (p. 319), cyanuric acid (p. 320) and ammelide (p. 325). When heated with water in a sealed tube at 180° C. or

when boiled with acids or alkalis it is decomposed into ammonia and carbon dioxide:

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3,$$
$$CO(NH_2)_2 + 2KOH = K_2CO_3 + 2NH_3,$$
$$CO(NH_2)_2 + 2HCl + H_2O = CO_2 + 2NH_4Cl.$$
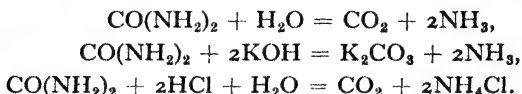
Urea acts as a very feeble mon-acid base, combining with one equivalent of an acid to form salts, most of which are soluble in water.

Urea reacts with ethyl diethyl malonate to form a condensation product known as **barbitone:**

| Urea | Ethyl di-ethyl malonate | Barbitone |
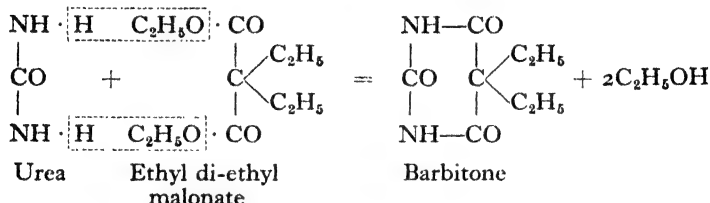
Urea also reacts with the acid chloride of diethyl malonic acid to form barbitone:

| Urea | Di-ethyl malonyl chloride | Barbitone |
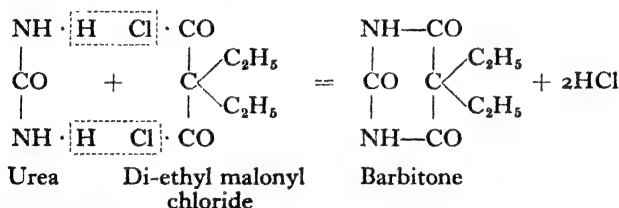
Barbitone is a white crystalline powder, m. pt. 191° C. It is odourless and has a faintly bitter taste. It is sparingly soluble in water, forming a neutral solution. It is soluble in alcohol, ether and chloroform, and in aqueous alkalis and carbonates.

When fused with sodium hydroxide it is decomposed

into ammonia, sodium carbonate and the sodium salt of di-ethyl acetic acid:

$$\begin{array}{c}\begin{array}{c}H-ONa\\H-ONa\\\\NH-CO\\\\CO\quad C\begin{array}{c}C_2H_5\\C_2H_5\end{array}\\\\NH-CO\\NaO-H\quad NaOH\\NaO-H\end{array}\end{array} = \begin{array}{c}C_2H_5\\C_2H_5\end{array}\!\!\!\!>\!\!CH\cdot COONa + 2Na_2CO_3 + 2NH_3$$

Sodium salt of
Di-ethyl acetic acid
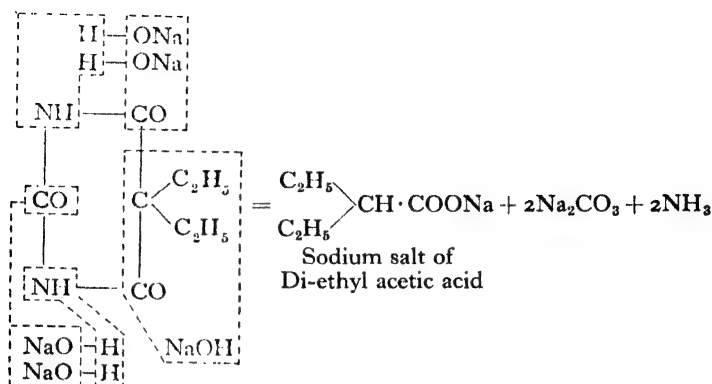
Barbitone is used in medicine in cases of sea-sickness, vomiting, &c., and as a soporific, under the name of **veronal**.

Reactions of Urea

1. *Biuret Reaction.* When urea is heated alone it yields ammonia, cyanuric acid, biuret and various other compounds. Biuret is obtained when urea is heated at about 155° C.

Experiment.—Heat a little (about 0·5 gm.) of solid urea over a very small flame in a dry test tube until it becomes liquid; bubbles of ammonia are evolved and tested by litmus paper:

$$2NH_2\cdot CO\cdot NH_2 = NH_2\cdot CO\cdot NH\cdot CO\cdot NH_2 + NH_3$$
Biuret
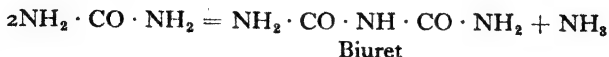
Continue to heat for two or three minutes until the liquid just solidifies; cool, dissolve in 10 c.c. of water, and add 1 c.c. of sodium hydroxide solution. To this solution add 1 drop of a 10 per cent solution of copper sulphate (B.P. method).

A reddish-violet solution is produced, which contains a compound of biuret with copper:

$$NH \left\langle \begin{matrix} C=(NH)-O \\ C=(NH)-O \end{matrix} \right\rangle Cu$$
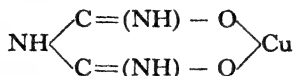
The biuret reaction is characteristic of the proteins and some of the more complicated polypeptides.

Further heating above 155° C. results in the formation of cyanuric acid:

$$3NH_2 \cdot CO \cdot NH_2 = 3NH_3 + H_3C_3N_3O_3$$
$$\text{Cyanuric acid}$$
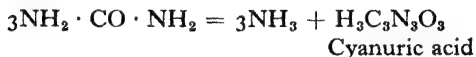
2. When a concentrated aqueous solution of urea is added to (a) concentrated nitric acid, (b) a concentrated solution of oxalic acid, urea nitrate and urea oxalate are obtained as white crystalline precipitates respectively. Urea nitrate is sparingly soluble in nitric acid:

$$CO(NH_2)_2 \cdot HNO_3; \quad [CO(NH_2)_2]_2 \cdot (COOH)_2 \cdot H_2O$$
$$\text{Urea nitrate} \qquad\qquad \text{Urea oxalate}$$
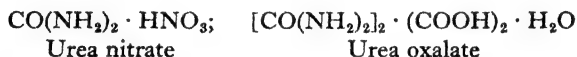
3. When a neutral solution of mercuric nitrate is added to a solution of urea, a white curdy precipitate—a basic compound of urea and mercuric nitrate—is obtained:

$$[CO(NH_2)_2]_2 \cdot Hg(NO_3)_2 \cdot 3HgO$$

4. When urea is boiled with sodium hydroxide solution, ammonia is evolved and sodium carbonate remains:

$$CO \left\langle \begin{matrix} NH_2 \\ NH_2 \end{matrix} \right. + \begin{matrix} HO \cdot Na \\ HO \cdot Na \end{matrix} = Na_2CO_3 + 2NH_3$$
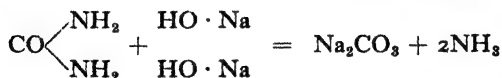
This reaction indicates that urea is an amide.

5. *Nitrous acid test.* To a solution of urea add a small

quantity of sodium nitrite and then dilute sulphuric acid. Warm gradually; carbon dioxide and nitrogen are evolved:

$$CO \begin{cases} N|O \cdot OH \\ \quad N|H_2 \\ \\ \quad N|H_2 \\ O| \quad N|OH \end{cases} = CO_2 + 2N_2 + 3H_2O$$
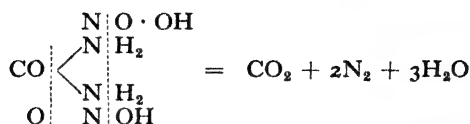
This reaction indicates that urea contains an —NH_2 group.

6. Heat with sodium in an ignition tube: a derivative of cyanamide is evolved. Extract with water and add excess of ammonia, then silver nitrate: a yellow precipitate of silver cyanamide, Ag_2CN_2, is formed.

7. *Methyl furil test.* Take a minute quantity of urea, mix with about an equal quantity of methyl furil solution in acetic acid and then treat with a drop of phosphorus oxychloride: a very brilliant blue colour develops.

8. Urea is decomposed by alkaline solutions of hypochlorites, hypobromites, or, better, by bromine water and sodium hydroxide solutions. On warming effervescence occurs and free nitrogen is rapidly evolved, the alkali retaining the carbon dioxide which is also liberated:

$$\begin{array}{c} \quad \quad \quad \quad \quad Na \quad Br \\ Na \\ \quad \quad > O + CO \begin{cases} N|H_2 + O| \\ \\ N|H_2 + O| \end{cases} = 3NaBr + N_2 + CO_2 + 2H_2O \\ Br \\ \quad \quad \quad \quad \quad Na \quad Br \end{array}$$
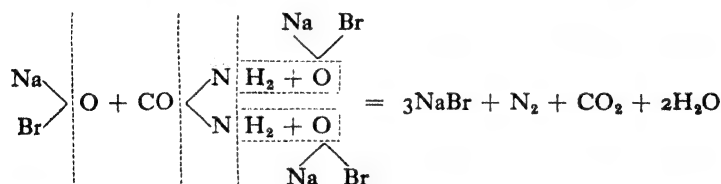
This reaction is utilized for the quantitative estimation of urea in urine for clinical purposes by measuring the volume of nitrogen evolved by the aid of Lunge's Nitrometer (p. 510).

Estimation of Urea.

This is performed:

1. By the Nitrometer method (see p. 513).
2. By the Ureometer (Hüfner's method).
3. By the Urease method (see p. 593).

The Ureometer is used to estimate urea in urine.

The urine is poured into the graduated limb A (fig. 37), and a measured volume is admitted into the central limb B by means of the tap T. The limb B is completely filled with sodium hypobromite solution, which reacts with the urea; nitrogen is liberated and collects in the top of the tube and is measured by the graduated scale. It should be noted that any ammonium salts present are also decomposed by the hypobromite solution with liberation of nitrogen. Hence these salts must be proved absent if the volume of nitrogen evolved is to be a correct measure of the amount of urea.

Fig. 37.—The Ureometer

$$CO(NH_2)_2 \equiv N_2$$
60 gm. urea $\equiv$ 22·4 litres nitrogen
$\therefore$ 1 c.c. $N_2 \equiv$ 0·0026786 gm. of urea.
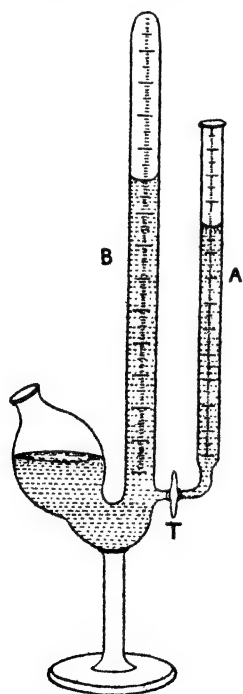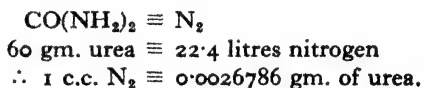
In the Urease method the enzyme present in the extracts of soya bean or of jack bean hydrolyses urea into ammonium carbonate, which is then estimated by means of standard acid.

$$CO(NH_2)_2 \equiv (NH_4)_2CO_3 \equiv 2HCl$$
60 gm. urea $\equiv$ 2000 c.c. $N \cdot HCl$
$\therefore$ 1 c.c. $N \cdot HCl \equiv$ 0·03 gm. of urea
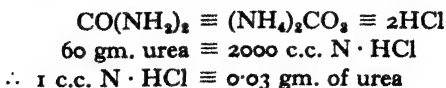
Uses.—Urea is made on a large scale for use as a fertilizer, by combining carbon dioxide and ammonia. It is used in smokeless powders and celluloid as a stabilizer. Certain medicinal remedies, e.g. veronal, are made from urea. It is a waste product in the digestive process; the nitrogenous matter in food, as —NH_2 group, is absorbed by the liver and excreted by the kidneys as urea. Outside the body urea undergoes fermentation and gives rise to products essential to plant life.
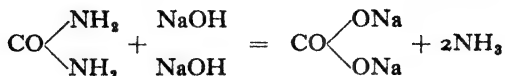
Constitution of Urea

The constitution of urea may be arrived at by reference to its methods of formation. Since urea is formed from carbonyl chloride and from ethyl carbonate, the reactions are analogous to those which take place in the formation of acetamide from acetyl chloride and from ethyl acetate:

$$CO \begin{cases} Cl \quad H \; NH_2 \\ \qquad + \\ Cl \quad H \; NH_2 \end{cases} = CO \begin{cases} NH_2 \\ NH_2 \end{cases} + 2HCl$$

cf. $$CO \begin{cases} CH_3 \\ Cl \end{cases} + \begin{matrix} HNH_2 \\ HNH_2 \end{matrix} = CO \begin{cases} CH_3 \\ NH_2 \end{cases} + NH_4Cl$$
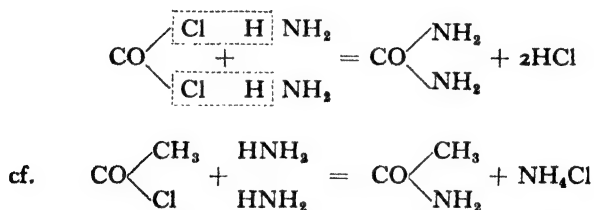
Urea may, therefore, be represented by the formula $CO(NH_2)_2$ and may be regarded as the di-amide of carbonic acid; hence the name carbamide. It may also be regarded as the amide of formamide:

$$CO \begin{cases} OH \\ OH \end{cases} \rightarrow CO \begin{cases} OH \\ H \end{cases} \rightarrow CO \begin{cases} NH_2 \\ H \end{cases} \rightarrow CO \begin{cases} NH_2 \\ NH_2 \end{cases}$$

|Carbonic acid|Formic acid|Form-amide|Carbamide|
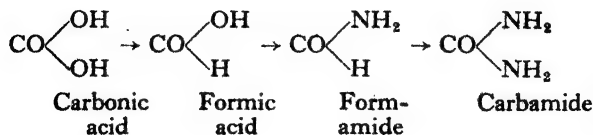
Its behaviour with boiling caustic alkalis, which decompose it into ammonia and a salt of carbonic acid, also shows that it is an amide:

$$CO\begin{cases} NH_2 \\ NH_2 \end{cases} + \begin{matrix} NaOH \\ NaOH \end{matrix} = CO\begin{cases} ONa \\ ONa \end{cases} + 2NH_3$$

Again, the presence of amido groups is shown by the action of nitrous acid.

Chattaway (1912) considered, however, that when ammonium cyanate is converted into urea an intermediate product, isocarbamide, is first formed, which then passes into the true amide. The reaction may be represented as follows:

$$NH_4-N=C=O \rightarrow HN=C=O + NH_3 \rightarrow$$
Ammonium cyanate

$$\rightarrow HN=C\begin{cases} OH \\ NH_2 \end{cases} \rightarrow CO\begin{cases} NH_2 \\ NH_2 \end{cases}$$
Iso-   Urea
carbamide
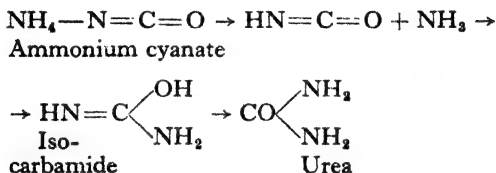
Werner (1914) concluded that ammonium cyanate has the normal structure $NH_4-O-C\equiv N$.

At low temperatures this exists in a state of equilibrium:

$$NH_4-O-C\equiv N \rightleftharpoons NH_3 + OH-C\equiv N$$
Normal or
Enol form

but at higher temperatures

$$NH_4-O-C\equiv N \rightarrow NH_3 + H-N=C=O$$
Iso or
Keto form
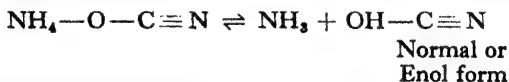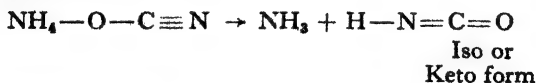
and the ammonia and the iso-form can react to produce urea, to which the following cyclic structure is given:

$$H-N=C=O + NH_3 = H-N=C\begin{cases} NH_2 \\ O \end{cases}$$
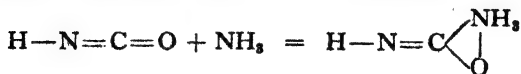
This formula is substantiated by the fact that when urea is heated it decomposes into ammonia and cyanic acid. The cyanic acid formed then reacts with the urea present to form biuret; this takes place at a temperature of 155° C.:

$$HN{=}C{\Large\langle}^{NH_2}_{OH} + HN{=}C{=}O \rightarrow HN{\Large\langle}^{\underset{|}{C}=NH}_{\underset{|}{C}=NH} \rightarrow HN{\Large\langle}^{\overset{O}{\overset{||}{C}}-NH_2}_{\underset{||}{\underset{O}{C}}-NH_2}$$
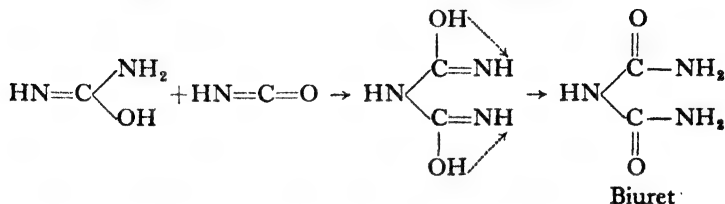
Biuret

When raised to a higher temperature some of the cyanic acid polymerizes into cyanuric acid:

$$3HN{=}C{=}O = H_3C_3N_3O_3$$
Cyanic   Cyanuric
acid   acid
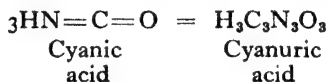
and the remainder probably reacts with the biuret to form ammelide:

$$NH{\Large\langle}^{CO-NH_2}_{CO-NH_2} + HN{=}C{=}O \rightarrow NH{\Large\langle}^{CO-NH}_{CO-NH}{\Large\rangle}C{=}NH + H_2O$$
Biuret   Ammelide
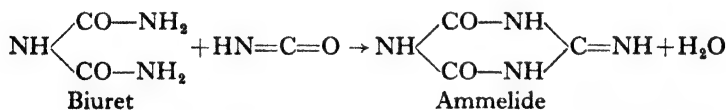
According to recent views urea has an enolic structure, that is, it contains an oscillatory hydrogen atom:

$$CO{\Large\langle}^{NH_2}_{NH_2} \rightleftharpoons HO-C{\Large\langle}^{NH}_{NH_2}$$
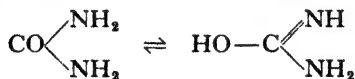
The formation of urea from ammonium cyanate, and the formations of cyanic acid, biuret, and ammelide can be more clearly explained by this structural representation of urea. Hence the name " carbamide " should not be used.

QUESTIONS

1. Give two methods of preparation and describe the general chemical properties of urea. How may it be converted into barbitone? (*Chemists and Druggists Qual.*)

2. Exhibit by means of formulæ the chemical relationship of carbonic acid, phosgene, and urea.

How may the percentage amount of urea be determined in dilute aqueous solution?

3. How may urea be prepared (*a*) from urine, (*b*) by synthesis, (*c*) from glucose?

What is the action on urea of (*a*) heat, (*b*) nitrous acid, (*c*) sodium hydroxide, (*d*) sodium hypochlorite?

4. How may amino-acetic acid and urea be synthesized? State the more important characteristics and reactions of these substances. (*Cambridge Higher School Cert.*)

CHAPTER XIII

Cyanogen Compounds

The simplest compounds of carbon in combination with nitrogen are hydrocyanic acid and cyanogen.

Hydrocyanic acid may be regarded as derived from methane, three hydrogen atoms being replaced by one trivalent nitrogen atom.

Cyanogen may similarly be regarded as a derivative of ethane:

$$CH_4 \longrightarrow HCN; \qquad CH_3CH_3 \longrightarrow CN \cdot CN$$

Methane　Hydrocyanic　Ethane　　　Cyanogen
　　　　　acid
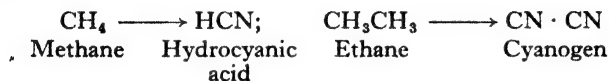
Most organic compounds containing nitrogen, when heated with sodium, give sodium cyanide. Potassium cyanide is formed when charcoal containing nitrogen is heated with potassium carbonate.

Cyanogen, $(CN)_2$.

Occurrence.—In coal gas, blast furnace gases and producer gas. The name cyanogen is derived from the Greek κύανος (*kuanos*), blue; γεννάω (*gennao*), to produce, owing to the fact that several of its compounds have a blue colour.

Formation.

1. By heating mercury or silver cyanide (Gay-Lussac method):

$$Hg(CN)_2 = Hg + (CN)_2$$

Mercuric　　　　　Cyanogen
cyanide
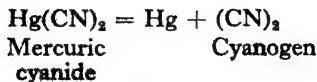
The cyanogen evolved may be ignited; it burns with a violet flame. The residue left contains in addition to a little mercury a black solid substance known as **paracyanogen,** $(CN)_n$, which is a polymer of cyanogen, for heat can reconvert it into cyanogen.

2. By heating concentrated solutions of potassium cyanide and copper sulphate:

$$4KCN + 2CuSO_4 = 2K_2SO_4 + Cu_2(CN)_2 + (CN)_2$$
$$(cf. \ 4KI + 2CuSO_4 = 2K_2SO_4 + Cu_2I_2 + I_2)$$
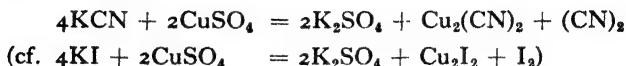
3. By dehydrating oxamide or anhydrous ammonium oxalate, by distillation with phosphorus pentoxide:

$$\begin{array}{ccc} CONH_2 & & CN \\ | & = & | & + 2H_2O \\ CONH_2 & & CN \end{array}$$
Oxamide
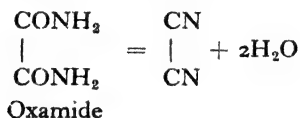
Experiment.—Place oxamide in a hard glass tube to a depth of about half an inch; add twice its volume of phosphorus pentoxide and mix thoroughly with a glass rod. Heat the tube gently; the cyanogen evolved can be ignited at the mouth of the tube.

Properties.—Cyanogen is a colourless, very poisonous gas which can be condensed to a colourless liquid, b. pt. $-21°$ C. Its odour is characteristic. It is readily soluble in water and in alcohol. The solution in water gradually undergoes a change and a brown amorphous substance known as *azulmic acid* is deposited. Other products such as ammonium oxalate, ammonium carbonate, urea, and hydrocyanic acid are also found in the aqueous solution:
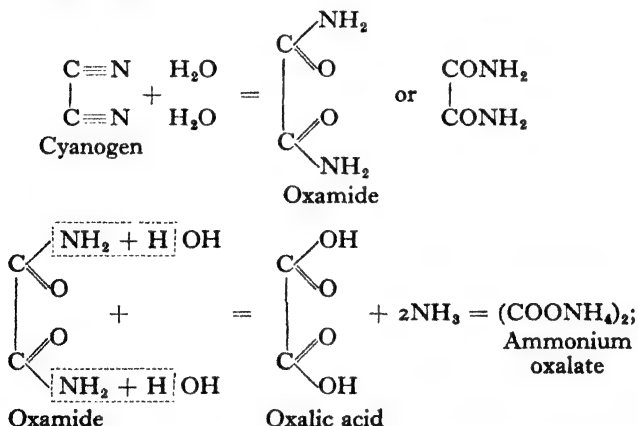
$$(CN)_2 + 4HOH = (COONH_4)_2$$
Ammonium oxalate
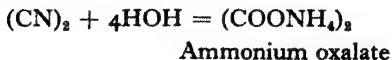
Cyanogen resembles the Halogens. It reacts with

a solution of potassium hydroxide, forming potassium cyanide and potassium cyanate:

$$(CN)_2 + 2KOH = KCN + KCNO + H_2O$$
$$(cf. \; Cl_2 + 2KOH = KCl + KClO + H_2O)$$
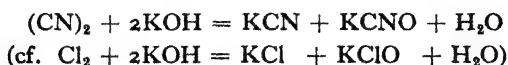
It also reacts with hydrogen to form hydrocyanic acid, HCN; the latter is analogous to the halogen acids, and its salts resemble the halides. Silver cyanide resembles silver chloride. It is precipitated from a solution of potassium cyanide by silver nitrate, and is soluble in ammonia.

Cyanogen also resembles chlorine in possessing diatomic molecules. When treated with hydrochloric acid it is first converted into oxamide and then into oxalic acid (and ammonium chloride):

$$
\begin{array}{c}
C\equiv N \\
| \\
C\equiv N
\end{array}
+
\begin{array}{c}
H_2O \\
H_2O
\end{array}
=
\begin{array}{c}
\quad\quad NH_2 \\
C \\
\quad\quad O \\
| \\
\quad\quad O \\
C \\
\quad\quad NH_2
\end{array}
\quad \text{or} \quad
\begin{array}{c}
CONH_2 \\
| \\
CONH_2
\end{array}
$$

Cyanogen   Oxamide

$$
\begin{array}{c}
\quad NH_2 + H\,OH \\
C \\
\quad O \\
| \\
\quad O \\
C \\
\quad NH_2 + H\,OH
\end{array}
\;+\;
=
\begin{array}{c}
\quad OH \\
C \\
\quad O \\
| \\
\quad O \\
C \\
\quad OH
\end{array}
+ 2NH_3 = (COONH_4)_2;
$$

Oxamide   Oxalic acid   Ammonium oxalate

these changes are the reverse of those which occur when ammonium oxalate is heated with phosphorus pentoxide (pp. 283, 285).

All substances which contain the cyanogen group behave in a similar manner, and are converted on hydrolysis into carboxylic acids or their salts, *amides* being formed as intermediate products. This is a very important general reaction.

Hydrocyanic Acid, Hydrogen Cyanide, Prussic Acid, HCN.

Occurrence.—Prussic acid is not found in Nature in the free state but usually in combination with glucose and benzaldehyde as **amygdalin**. Amygdalin is a crystalline compound known as a **glucoside** and is found in many plants, either in the leaves, as in those of the laurel, or in the kernels of many stone fruits, as in the plum and cherry.

The term **glucoside** is applied to all those vegetable products which, on treatment with acids or alkalis, yield a sugar (or some closely allied carbohydrate) and some other substances as decomposition products, such as phenols or aromatic aldehydes (pp. 354, 355).

Formation.

1. By the hydrolysis of amygdalin, either with dilute sulphuric acid, or by the action of the enzyme *emulsin* which occurs in bitter almonds:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_6H_5CHO + HCN + 2C_6H_{12}O_6$$

Amygdalin   Benzal-   Hydro-   Glucose
                     dehyde   cyanic
                              acid
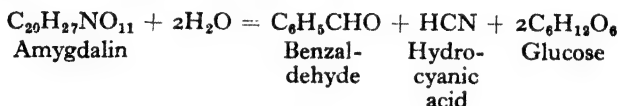
2. By decomposing metallic cyanides with hydrochloric acid or moderately strong sulphuric acid:

$$KCN + HCl = KCl + HCN$$

The vapours are passed through a U-tube containing calcium chloride to dry the gas, and then through another U-tube surrounded by ice to condense the vapours. In this way pure anhydrous hydrocyanic acid is obtained.

3. By heating chloroform with alcoholic ammonia and potassium hydroxide:

$$CHCl_3 + NH_3 + 4KOH = KCN + 3KCl + 4H_2O;$$
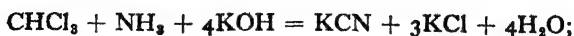
the potassium cyanide is then treated as above.

4. *Laboratory Method.* By distilling potassium ferro-cyanide with dilute sulphuric acid:

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 3K_2SO_4 + K_2Fe[Fe(CN)_6] + 6HCN$$

Experiment. To prepare hydrocyanic acid.

This experiment should be performed in a fume cupboard and on no account should the vapours be inhaled as they are **extremely poisonous.**

Required:

125 gm. powdered potassium ferrocyanide.
150 c.c. water.
50 c.c. concentrated sulphuric acid.

A 500 c.c. distilling flask is connected to a Liebig condenser, the far end of the condenser being connected to a receiver cooled in ice. The receiver consists of a wide-mouthed bottle fitted with a two-hole cork; the condenser is connected to one hole, while the other is provided with a long piece of glass tubing reaching to the flue opening. All connexions are tested for leakage. The ferrocyanide is then introduced into the flask and dissolved in the water, the strong acid is cautiously poured in, and the mixture is gently distilled over a wire gauze. About 20 c.c. of hydrocyanic acid of 50 per cent strength are collected in the bottle. This acid may be purified by redistillation from solid calcium chloride.

5. By heating ammonium formate with phosphorus pentoxide:

$$H \cdot COONH_4 = HCN + 2H_2O$$

Properties.—Colourless, very volatile liquid, b. pt. 26° C., m. pt. −12° C. It has a very characteristic odour of bitter almonds (do not inhale). It is inflammable, and burns with a violet flame:

$$4HCN + 5O_2 = 2N_2 + 4CO_2 + 2H_2O$$

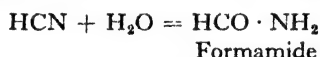It is **extremely poisonous,** even in the smallest quantity.

Antidotes include hydrogen peroxide, or better, freshly precipitated ferrous hydroxide; or ammonia (inhaled).

Hydrocyanic acid dissolves in water in all proportions; the solution is known as **prussic acid.** It is one of the weakest acids and scarcely reddens blue litmus. Its salts are decomposed by carbon dioxide.

Pure hydrocyanic acid is stable, but its aqueous solution decomposes, giving ammonium formate and oxalate and brown amorphous products. A small quantity of a mineral acid delays this decomposition:

$$HCN + 2H_2O \rightleftharpoons H \cdot COONH_4$$
<div align="center">Ammonium
formate</div>
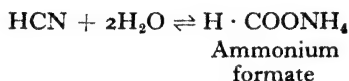
It is acted on by concentrated hydrochloric acid with the formation of formic acid and ammonium chloride. The reaction proceeds with considerable evolution of heat, formamide being formed as an intermediate product:

$$HCN + H_2O = HCO \cdot NH_2$$
<div align="center">Formamide</div>

$$HCO \cdot NH_2 + HCl + H_2O = H \cdot COOH + NH_4Cl$$
<div align="center">Formic acid</div>
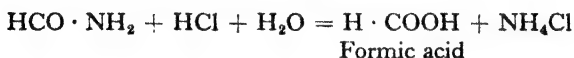
When concentrated sulphuric acid acts on hydrocyanic acid, formic acid is not produced owing to the dehydrating action of the sulphuric acid; the final product is carbon monoxide.

Boiling alkalis also convert hydrocyanic acid into formic acid and ammonia:

$$HCN + 2HOH = HCOOH + NH_3$$
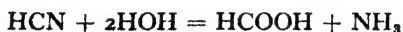
Hydrocyanic acid yields formamide on hydrolysis, and the reverse process may be effected by removing the elements of water from formamide by distilling it with phosphorus pentoxide:

$$H \cdot CO \cdot NH_2 - HOH = HCN$$

Methylamine is formed on the reduction of an alcoholic solution of hydrocyanic acid with metallic sodium, just as methyl cyanide is converted into ethylamine. The reduction may also be brought about with zinc dust and hydrochloric acid:

$$HCN + 2H_2 = CH_3 \cdot NH_2$$
$$(cf.\ CH_3CN + 2H_2 = CH_3 \cdot CH_2 \cdot NH_2)$$
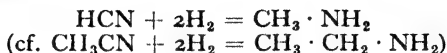
It is a weak monobasic acid, reacting with bases and basic oxides to form salts known as *cyanides*. It combines directly with most aldehydes and ketones to form cyanhydrins:

$$
\begin{array}{ccc}
\overset{\displaystyle H}{\underset{\displaystyle |}{\ }} & & \overset{\displaystyle H}{\underset{\displaystyle |}{\ }} \\
CH_3-C=O + H & = & CH_3-C-OH \\
\underset{\displaystyle |}{\ } & & \underset{\displaystyle |}{\ } \\
CN & & CN
\end{array}
$$

Acetaldehyde   Ethylidene
                        cyanhydrin
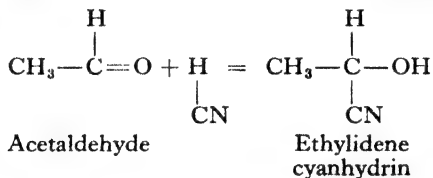
On hydrolysis these cyanhydrins are converted into hydroxy-acids (pp. 246, 266).

Constitution of Hydrocyanic Acid.

This has not yet been determined with certainty. It may be either

$$
\underset{\text{I}}{H-C\equiv N} \quad \text{or} \quad \underset{\text{II}}{H-N=C} \quad \text{or} \quad \underset{\text{III}}{H-N=C=}
$$

thus exhibiting *Tautomerism*. In the second formula the carbon is represented as a dyad element, as it is in carbon monoxide $C=O$. The first formula has the following evidence in its favour:

1. Formation of hydrocyanic acid from ammonium formate.

2. Conversion into formic acid when heated with alkalis:

$$
H-C\equiv\underset{\underset{\displaystyle H}{\displaystyle N}}{\ } + \underset{\underset{\displaystyle OH}{\displaystyle O}}{H_2} = H-C\underset{\displaystyle OH}{\overset{\displaystyle O}{\big\langle}} + NH_3
$$
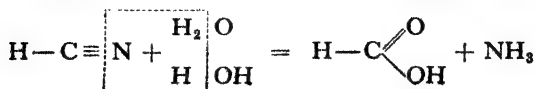
Uses.—A very dilute aqueous (2 per cent) solution is used in medicine. A concentrated aqueous solution of the gas, and also the gas itself, is used to kill insects, vermin, &c., and for fumigation after infectious diseases. It is used in synthesis, e.g. in the preparation of the hydroxy-acids from aldehydes and ketones (see above).
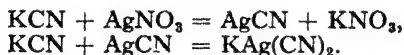
Cyanides.

Hydrocyanic acid forms a series of salts called *cyanides*, analogous to the chlorides formed from hydrochloric acid. The cyanides are prepared by the action of alkali and certain other metallic hydroxides on the acid. Carbonates do not react with the acid. The cyanides of the alkali metals and alkaline earth metals, and mercuric cyanide, are soluble in water.

Mercuric cyanide, $Hg(CN)_2$, is usually prepared by the action of hydrocyanic acid on mercuric oxide. This salt possesses the property of being non-ionized in aqueous solution, hence it gives no test either for mercury or for a cyanide.

The cyanides of the heavy metals form double cyanides, some of which are important. For instance, when potassium cyanide is added to solutions of salts of heavy metals, the precipitated cyanide which first forms redissolves on addition of a slight excess of the alkali cyanide:

(*a*) Potassium argentocyanide:

$$KCN + AgNO_3 = AgCN + KNO_3,$$
$$KCN + AgCN = KAg(CN)_2.$$

(*b*) Potassium ferricyanide:

$$3KCN + FeCl_3 = Fe(CN)_3 + KCl,$$
$$3KCN + Fe(CN)_3 = K_3Fe(CN)_6.$$

The alkali double cyanides are all soluble in water.

Sodium cyanide, NaCN, is the most important of all the cyanides, owing to the fact that it dissolves gold from

gold-bearing quartzose rock. It is usually converted into the potassium salt for this purpose. The extraction is known as the *cyanide* or *MacArthur-Forrest Process* (p. 337). Sodium cyanide is also used in gold and silver electroplating and in the manufacture of synthetic indigo.

Formation.

1. *Commercial Method.* (A) By passing dry ammonia over metallic sodium contained in iron retorts at about 350° C.; sodamide is formed. The temperature must be kept low, as sodamide decomposes into the elements at 500° C.

$$2Na + 2NH_3 = 2NaNH_2 + H_2$$
$$\text{Sodamide}$$
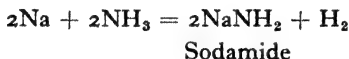
Sodamide is a white solid when pure (m. pt. 210° C.).

The fused sodamide is poured on to hot charcoal, the temperature being kept between 350° C. and 600° C.; sodium cyanamide is then formed:

$$2NaNH_2 + C = Na_2CN_2 + 2H_2$$
$$\text{Sodium}$$
$$\text{cyanamide}$$
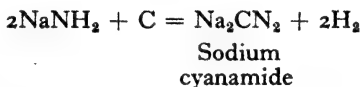
The temperature is then raised to about 750° C., when the cyanamide reacts with additional carbon to form sodium cyanide:

$$Na_2CN_2 + C = 2NaCN$$
$$\text{Sodium cyanide}$$
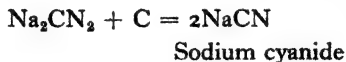
The fused mass is then filtered from small quantities of solid impurities, when a very pure sodium cyanide is obtained.

An impure sodium cyanide (about 40 per cent) is made by fusing commercial calcium cyanamide with sodium chloride. Commercial cyanamide made by the action of

nitrogen on calcium carbide always contains carbon and is known as " nitrolim ":

$$CaCN_2 + C + 2NaCl = 2NaCN + CaCl_2$$
Calcium
cyanamide
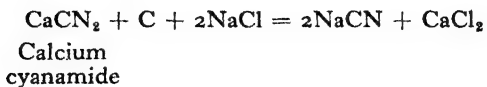
(B) From coal gas, which contains hydrocyanic acid and ammonia. These gases are passed into a solution of copper chloride and the ammonium cuprocyanide formed is decomposed with dilute sulphuric acid. The hydrogen cyanide evolved during the reaction is passed into sodium hydroxide to form sodium cyanide:

$$4HCN + 4NH_3 + Cu_2(CN)_2 = 2(NH_4)_2Cu(CN)_3,$$
$$2(NH_4)_2Cu(CN)_3 + 2H_2SO_4 = 2(NH_4)_2SO_4 + 4HCN + Cu_2(CN)_2,$$
$$HCN + NaOH = NaCN + H_2O.$$
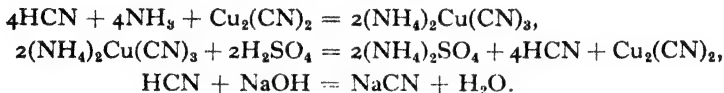
2. By heating sodium ferrocyanide, obtained in coal-gas manufacture, with metallic sodium:

$$Na_4Fe(CN)_6 + 2Na = 6NaCN + Fe$$

The fused mass is then filtered from the finely divided iron.

3. By passing ammonia over a heated or a fused mixture of sodium carbonate and charcoal:

$$2NH_3 + Na_2CO_3 + C = 2NaCN + 3H_2O$$

4. By passing nitrogen at a high temperature over barium carbide. The barium cyanide is then heated with sodium carbonate in aqueous solution. Barium carbonate is precipitated and filtered off, and the filtrate evaporated to dryness:

$$N_2 + BaC_2 = Ba(CN)_2,$$
$$Ba(CN)_2 + Na_2CO_3 = 2NaCN + BaCO_3.$$
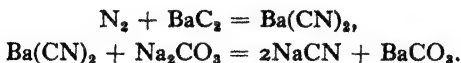
Properties.—Sodium cyanide is **extremely poisonous** and great care should be taken in working with it. It

dissolves readily in water and the solution has an alkaline reaction, owing to partial hydrolysis:

$$NaCN + HOH \rightleftharpoons NaOH + HCN$$
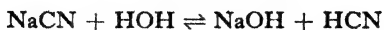
On boiling an aqueous solution of sodium cyanide, sodium formate is formed and ammonia is evolved:

$$NaCN + 2HOH = H \cdot COONa + NH_3$$
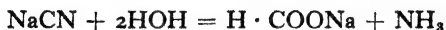
This reaction is important, as it is used for the preparation of sodium formate and formic acid.

The alkali cyanides are readily decomposed by inorganic and organic acids, evolving hydrocyanic acid. Even the carbon dioxide of the air decomposes the salt and sets free the acid, and hence the salt has the odour of hydrocyanic acid.

Sodium cyanide is used to dissolve gold, and large quantities are now used to extract gold from gold quartz. Only a 0·35 per cent solution is necessary to effect solution of gold in the presence of atmospheric oxygen:

$$2Au + 4NaCN + H_2O + O = 2NaAu(CN)_2 + 2NaOH$$

The gold is then deposited from the solution by electrolysis or by passing the sodium aurocyanide solution through perforated wooden boxes containing zinc turnings:

$$2NaAu(CN)_2 + Zn = Na_2Zn(CN)_4 + 2Au$$
Sodium   Sodium
aurocyanide   zincocyanide
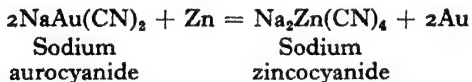
The slight excess of zinc used is dissolved out with dilute sulphuric acid. Nearly five million ounces of gold are extracted by this process annually.

Sodium cyanide is used in quantitative analysis and also in the preparation of organic compounds, such as veronal (p. 319) and synthetic indigo.

Potassium Cyanide is formed by the same reactions

as sodium cyanide.   In addition it can be produced by fusing potassium ferrocyanide either alone or with potassium carbonate, but this method is not used commercially:

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2;$$
$$K_2CO_3 + K_4Fe(CN)_6 = 5KCN + CO_2 + Fe + KCNO.$$

Its properties are similar to those of sodium cyanide.

Fused potassium cyanide is a powerful reducing agent, liberating metals from many metallic oxides:

$$KCN + PbO = KCNO + Pb$$

Detection of Hydrocyanic Acid and Cyanides.

1. Smell of bitter almonds **(dangerous poison)**.

2. Add nitric acid to a soluble cyanide and warm; hydrocyanic acid is evolved. A drop of silver nitrate solution on a watch-glass or glass rod in contact with the vapour becomes turbid, owing to the formation of silver cyanide.

3. Make the solution alkaline with potash, add a few drops of ferrous sulphate and one drop of ferric chloride solution and boil.   Then acidify the solution;   a precipitate of Prussian Blue is formed.

4. To the solution add yellow ammonium sulphide and evaporate to dryness.   Dissolve the residue of ammonium sulphocyanide, NH_4CNS, in water or dilute hydrochloric acid and add a drop of ferric chloride solution; a deep red colour of ferric sulphocyanide (thiocyanate) is imparted to the solution.

If the cyanide is mixed with substances which would interfere with the above reaction, the mixture is first distilled along with a little non-volatile organic acid, such as tartaric acid.   The distillate contains the hydrocyanic acid and is used for the tests.

Alkyl Derivatives of Hydrocyanic Acid

In addition to the metallic cyanides, prussic acid yields two classes of isomeric derivatives by the exchange of its hydrogen atom for alkyl radicles:

A. **Alkyl cyanides** or **nitriles,** $R—C≡N$;

B. **Isocyanides, Isonitriles,** or **Carbylamines,**

$$R—N=C \quad \text{or} \quad R—N≡C,$$
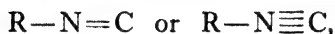
where R is an alkyl radicle $—CH_3$, $—C_2H_5$, &c.

These compounds cannot be regarded as true esters of prussic acid, as they are not hydrolysed to the acid and alcohol (see p. 342).

A. The **Alkyl Cyanides** are either colourless liquids or solids. They have an ethereal odour and volatilize without decomposition. They are lighter than water, usually stable, the lower members being soluble in water. Their boiling-points are similar to those of the corresponding alcohols and they are decomposed by alkalis.

Methyl Cyanide, Acetonitrile, CH_3CN, illustrates the formation and reactions of this class of compounds.
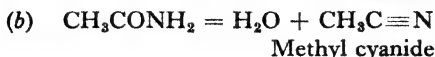
Formation.

1. By distilling potassium cyanide with either methyl iodide or potassium methyl sulphate or dimethyl sulphate:
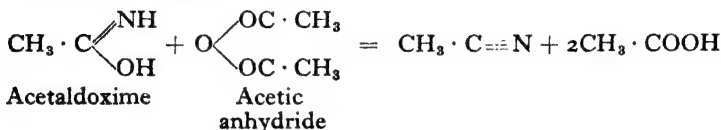
(a) $\quad CH_3I + KCN = KI + CH_3CN$

(b) $\quad \begin{matrix} CH_3 \\ K \end{matrix} \Big> SO_4 + KCN = K_2SO_4 + CH_3CN$

(c) $\quad \begin{matrix} CH_3 \\ CH_3 \end{matrix} \Big> SO_4 + KCN = \begin{matrix} CH_3 \\ K \end{matrix} \Big> SO_4 + CH_3CN$
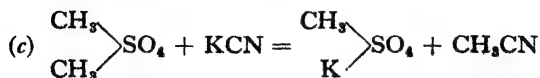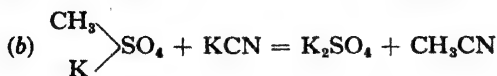
2. By distilling the ammonium salt or the amide of a

fatty acid and treating the amide with a dehydrating agent, such as phosphorus pentoxide:

(a) $CH_3COONH_4 = H_2O + CH_3CONH_2$
Acetamide

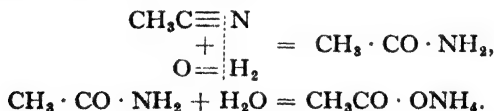(b) $CH_3CONH_2 = H_2O + CH_3C\equiv N$
Methyl cyanide

The name acetonitrile is given to methyl cyanide, owing to this method of formation from acetic acid.

3. By warming acetaldoxime with either acetic anhydride or acetyl chloride:

$$CH_3 \cdot C{\overset{NH}{\underset{OH}{\Big<}}} + O{\overset{OC \cdot CH_3}{\underset{OC \cdot CH_3}{\Big<}}} = CH_3 \cdot C\!\!=\!\!N + 2CH_3 \cdot COOH$$

Acetaldoxime   Acetic
anhydride

Properties.—Methyl cyanide is found in the products of distillation of vinasse (beet sugar residues), and in coal tar. It is a colourless liquid, b. pt. 81·6° C. It burns in air with a luminous flame. It dissolves in water.

Reactions.—1. On hydrolysis with acids or alkalis it is converted into ammonium acetate, acetamide probably being formed as an intermediate product:
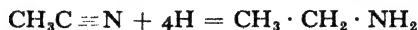
$$\begin{array}{c} CH_3C\equiv N \\ + \\ O=H_2 \end{array} = CH_3 \cdot CO \cdot NH_2,$$

$$CH_3 \cdot CO \cdot NH_2 + H_2O = CH_3CO \cdot ONH_4.$$

With excess of alkali the ammonium salt is decomposed and ammonia is evolved.

This reaction is important as showing the conversion of a —CN group into a —COOH group and the possibility of converting saturated alcohols, $C_nH_{2n+1}OH$, into aliphatic acids, $C_nH_{2n+1}COOH$, containing one atom of carbon more than the alcohol contains (p. 158):

e.g. $CH_3OH \rightarrow CH_3I \rightarrow CH_3CN \rightarrow CH_3COOH$
Methyl alcohol   Acetic acid
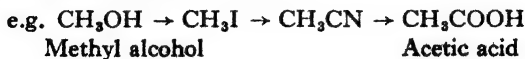
2. By reduction (with sodium and alcohol) it is converted into a primary amine:
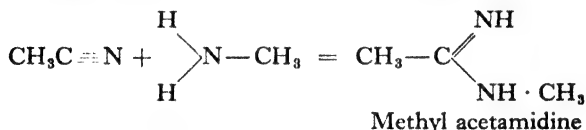
$$CH_3C \equiv N + 4H = CH_3 \cdot CH_2 \cdot NH_2$$

3. It combines with hydrochloric acid and the halogens to form additive compounds, amido and imido chlorides being formed:
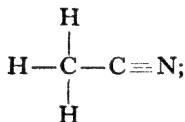
$$CH_3C \equiv N + 2HCl = CH_3 - C \cdot Cl_2 - NH_2,$$
<div align="center">Acet-amido chloride</div>

$$CH_3C \cdot N + HCl = CH_3 - C \cdot Cl = NH.$$
<div align="center">Acet-imido chloride</div>

The halogen additive compounds are easily decomposed.

4. It reacts with amines to form amidines:

$$CH_3C \equiv N + \overset{H}{\underset{H}{\Big\rangle}}N - CH_3 = CH_3 - C\overset{NH}{\underset{NH \cdot CH_3}{\diagdown}}$$

<div align="center">Methyl acetamidine</div>

Constitution of Methyl Cyanide.

The constitution of methyl cyanide is

$$H - \overset{\overset{\displaystyle H}{\displaystyle |}}{\underset{\underset{\displaystyle H}{\displaystyle |}}{C}} - C \equiv N;$$

that is, the carbon atoms are directly linked to one another and one carbon atom is linked to a methyl group and also to a nitrogen atom. This is supported by the facts that when methyl cyanide is hydrolysed, acetic acid is formed, which contains a —CH$_3$ group directly linked to a carbon atom in the carboxyl group, and when methyl cyanide is hydrolysed with an alkali the nitrogen is eliminated as ammonia.

B. The **Isocyanides** are colourless liquids soluble in alcohol and in ether but sparingly soluble in water. They have a faint alkaline reaction and an intolerable smell and are poisonous. Their boiling-points are lower than those of the corresponding isomeric nitriles. They are very stable towards alkalis.

Methyl Isocyanide, CH_3NC, will serve to illustrate the characteristics of this class of compound.

Formation.

1. By heating together methyl (i.e. alkyl) iodide with silver cyanide (not potassium cyanide); a double compound with silver cyanide is formed as an intermediate product:

$$Ag \cdot N = C + CH_3I = \overset{Ag}{\underset{I}{CH_3}} N = C = AgI + CH_3N = C$$
$$\text{Methyl}$$
$$\text{carbylamine}$$
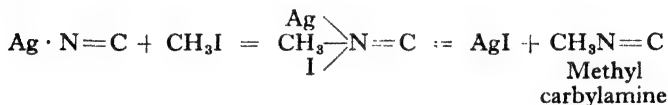
2. By the action of chloroform and alcoholic potash on methylamine (i.e. a primary amine):

$$CH_3NH_2 + CHCl_3 + 3KOH = CH_3N = C + 3KCl + 3H_2O$$
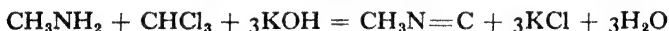
Properties.—Methyl isocyanide is a colourless poisonous liquid with an intolerable smell, b. pt. $59.6°$ C.

Reactions.—1. On hydrolysis with hot water or cold acids, formic acid is produced, together with a primary amine which contains one carbon atom less than the isonitrile from which it is formed:

$$CH_3N = C + 2HOH = CH_3NH_2 + HCOOH$$

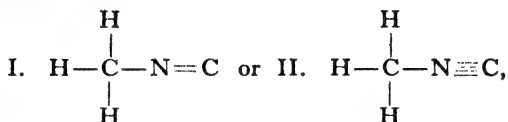Alkalis do not decompose methyl isocyanide, so cannot be used for its hydrolysis (contrast methyl cyanide).

2. Methyl isocyanide forms additive compounds with the halogens, hydrochloric acid, &c., which differ from those of methyl cyanide.

3. It is reduced by nascent hydrogen to a secondary amine:

$$CH_3 - N = C + 4H = CH_3 - NH - CH_3$$

Dimethylamine
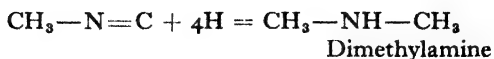
Constitution of Methyl Isocyanide.

The constitution of methyl isocyanide is

$$\text{I.} \quad H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - N = C \quad \text{or} \quad \text{II.} \quad H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - N \equiv C,$$

that is, the —CH_3 group is directly linked to the N atom. This is supported by reactions 1 and 3 above, i.e. the production of formic acid from the end carbon atom and the production of a secondary amine on reduction. Formula I is usually accepted as the correct constitution for an isocyanide, although the end carbon atom in this compound is divalent, contrary to the accepted tetravalency of carbon. Divalency is shown by the fact that compounds of the following structure are known:

$$CH_3N = C = O; \quad C_2H_5N = C = Cl_2, \text{ &c.}$$

The characteristic reactions of methyl cyanide and methyl isocyanide make it abundantly clear that hydrocyanic acid exhibits tautomerism.

Poison Gases.

In view of the widespread interest that is being taken to-day in the subject of poison gases (e.g. HCN) and the precautions that may be necessary to safeguard the civil population in the event of such gases being used in warfare, the student should consult the scheme of analysis for their detection adopted by Studinger, as outlined in *Chemistry and Industry*, Vol. 56, No. 10, (1937).

Studinger's classification of poison gases is as follows:

Class I.—*Gases resembling chlorine only.*

Tear and blister gases (xylyl bromide, mono- and tri-chloro-acetophenone, &c.).

Choking gases, such as perchloroformic ester. (Phosgene and chlorine are also included.)

Class II.—*Gases containing chlorine and sulphur.*

Dichlorodiethyl sulphide (mustard gas).

Class III.—*Gases containing chlorine and nitrogen.*

Choking gases, such as dichloroformoxime, chloropicrin. (Hydrogen cyanide is also included).

Class IV.—*Gases containing chlorine and arsenic.*

Nose and throat irritants: arsines; blister gases. Lewisite (chloro-vinyl-dichloro-arsine).

Class V.—*Gases containing metals.*

Iron carbonyls; lead tetra-alkyls.

QUESTIONS

1. How would you prepare a strong solution of hydrocyanic acid? Give two distinctive tests for this substance. What is its behaviour towards (*a*) sulphuric acid, (*b*) aldehyde, (*c*) mercuric oxide? (*Pre. Med.*)

2. By what chemical changes would you effect the following exchanges in organic substances:

(*a*) —OH for —NH_2,
(*b*) —NH_2 for —OH,
(*c*) —OH for —COOH,
(*d*) —COOH for —OH,
(*e*) —COOH for —CN,
(*f*) —CN for—COOH?

3. Give at least one example of each of the following: an acetal, a chlorhydrin, a cyanhydrin, a cyanide (nitrile). Indicate how *two* of the above may be prepared.

4. Describe with examples the purposes for which the following reagents are employed in organic chemistry:

(*a*) hydriodic acid,
(*b*) phosphorus pentachloride,
(*c*) nitrous acid,
(*d*) hydrocyanic acid.

(Chemists and Druggists Qual.)

5. Starting with calcium carbide, by what reactions may acetaldehyde, acetic acid, benzene, urea, and sodium cyanide be prepared?

6. Describe the preparation of formic acid. How is it related to (*a*) hydrogen cyanide, (*b*) chloroform? How would you prepare a specimen of oxalic acid from formic acid? In what respects do formates (*a*) resemble, (*b*) differ from oxalates?

(Oxford Higher School Cert.)

7. Illustrate, by reference to examples, what you understand by: hydrolysis, condensation, polymerization, tautomerism.

8. State the products obtained by the hydrolysis of each of the following: ethyl hydrogen sulphate, ethylidene chloride, acetamide, methyl cyanide.

Mention the hydrolysing agent you would employ in each case.

9. How is sodium (or potassium) cyanide produced on the large scale, and for what purposes is it employed? How does it react with alkyl halides, and how are the resulting compounds used in organic syntheses? *(Oxford Higher School Cert.)*

10. Give examples to illustrate the use made of each of the following reagents in organic practice: bromine, hydrogen cyanide, hydriodic acid, phosphorus pentachloride.

The Carbohydrates

The name carbohydrate is given to those substances which are composed of carbon together with hydrogen and oxygen in the proportion to form water. Their general formula may be represented as

$C_x(H_2O)_n$; x is usually 6 or 12; n usually 6 or 11.

The name, however, is inaccurate, as there are substances such as formaldehyde CH_2O, acetic acid $C_2H_4O_2$, lactic acid $C_3H_6O_3$, which contain hydrogen and oxygen in the proportion to form water and yet are not reckoned to be carbohydrates. Moreover, there are a few carbohydrates which contain hydrogen and oxygen in a different proportion, e.g. rhamnose, $C_6H_{12}O_5$.

A typical carbohydrate contains six carbon atoms or a multiple of six, but some contain a smaller number of carbon atoms.

Classification of the Carbohydrates.

The carbohydrates may be divided into two classes:

1. **The Sugars,** which are sweet and crystalline substances and are subdivided into:

(*a*) **Simple Sugars**, Monoses, or Monosaccharoses, which cannot be hydrolysed and which are again subdivided into: Trioses, Tetroses, Pentoses, &c., according to the number of oxygen atoms contained in them.

(*b*) **Complex Sugars,** which are subdivided into: Disaccharoses and Trisaccharoses, and can be hydrolysed.

2. **The Polysaccharoses,** or Polyoses, which are

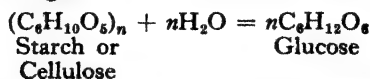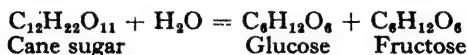complex carbohydrates, tasteless and non-crystalline, and can be hydrolysed.

The termination **-ose** is reserved for the Sugars.

The following list contains the more important carbohydrates, and as most of them are optically active in solution the positive sign $+$ and negative sign $-$ have been inserted to show whether the carbohydrate is dextro-rotatory or lævo-rotatory. The symbols A and K indicate whether the monoses are aldehydes or ketones:

<div align="center">CARBOHYDRATES</div>

Simple Sugars	Complex Sugars	Polyoses
Monosaccharoses (a) *Pentoses* ($C_5H_{10}O_5$)	*Disaccharoses* $C_{12}H_{22}O_{11}$	*Polysaccharoses* ($C_6H_{10}O_5$)$_n$
Arabinose $+$ A Xylose $+$ A Ribose $+$ A	Sucrose or Cane sugar $+$ Lactose or Milk sugar $+$	Cellulose $+$ Starch $+$
(b) *Hexoses* ($C_6H_{12}O_6$)	Maltose or Malt sugar $+$	Glycogen $+$ Dextrin $+$
Glucose $+$ A Fructose $-$ K Mannose $+$ A Galactose $+$ A	*Trisaccharoses* $C_{18}H_{32}O_{16}$ Raffinose $+$ Gentianose $+$	Inulin $-$ Gums

The complex sugars and polyoses give the simple sugars on hydrolysis with dilute acids. Thus cane sugar is converted into a mixture of glucose and fructose, and starch and cellulose are both converted into glucose.

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
<div align="center">Cane sugar   Glucose   Fructose</div>

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6$$
<div align="center">Starch or   Glucose
Cellulose</div>

A few of the more common carbohydrates are discussed below.

The Simple Sugars

The monosaccharoses are all open-chain hydroxy-aldehydes or hydroxy-ketones; they contain from 3 to 9 oxygen atoms in the molecule. The hexoses only will be considered here.

The sugars which contain the aldehyde group, —CHO, are known as **aldoses**; those which contain the ketone or carbonyl group, $>$CO, are called **ketoses**. Glucose is an aldose and fructose a ketose. Their structural formulæ are as follows:

CH$_2$OH
|
CH · OH   CH$_2$OH
| |
CH · OH   (CHOH)$_4$
| or |
CH · OH   CHO
|
CH · OH

|
CHO
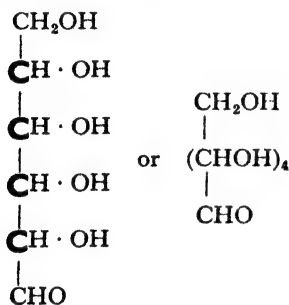
Glucose or Aldo-hexose

Contains 4 asymmetric carbon atoms, hence there are $2^4 = 16$ possible stereo-isomers.

CH$_2$OH
|
CHOH   CH$_2$OH
| |
CHOH   (CHOH)$_3$
| or |
CHOH   CO
| |
CO   CH$_2$OH
|
CH$_2$OH
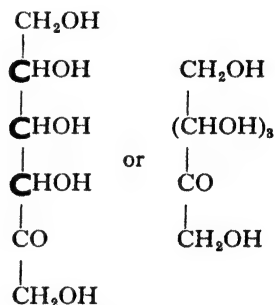
Fructose or Keto-hexose

Contains 3 asymmetric carbon atoms, hence there are $2^3 = 8$ possible stereo-isomers.

Glucose, Grape Sugar, or **Dextrose** is found in large quantities in grapes (hence the name grape sugar) in the nectar of flowers, and in ripe fruit. The name glucose is from the Greek γλυκύς (*glukus*), sweet, on account of its sweet taste, and the name dextrose from its dextro-rotation, but this name has now been discarded owing to the preparation of a lævo-dextrose.

Glucose occurs regularly in small quantities in the blood lymph and in human urine. In the disease *diabetes mellitus* the amount of glucose found in the urine may rise to 12

per cent, corresponding to an excretion of over 500 gm. a day. It is found in the free state in the white and yolk of eggs and in the combined state in many glucosides (p. 355). Glucose is one of the products of the hydrolysis of glucosides with either dilute mineral acids or certain enzymes.
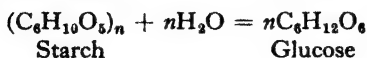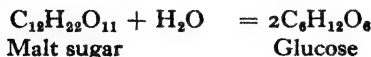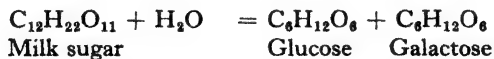
Formation.

1. By the hydrolysis of cane sugar with dilute acids or the enzyme *Invertase*:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
$$\text{Cane Sugar} \qquad\qquad \text{Glucose} \quad \text{Fructose}$$
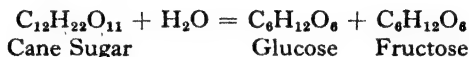
Experiment.—Pour 500 c.c. of 90 per cent alcohol or methylated spirit into a litre flask and add 20 c.c. of concentrated hydrochloric acid. Heat the mixture to 45–50° C. Then add 175 gm. of powdered cane sugar a little at a time with constant stirring. Keep the mixture at about 50° C. for two hours, then cool. When the solution is cold either stir or introduce a crystal of glucose to promote crystallization. After two days filter and wash the crystals with alcohol. Recrystallize from 80 per cent alcohol. Fructose, formed at the same time, is more soluble in alcohol than glucose, and so remains in solution.

2. By the hydrolysis of milk sugar, malt sugar, starch, cellulose, &c.:

$$C_{12}H_{22}O_{11} + H_2O \quad = C_6H_{12}O_6 + C_6H_{12}O_6$$
$$\text{Milk sugar} \qquad\qquad \text{Glucose} \quad \text{Galactose}$$

$$C_{12}H_{22}O_{11} + H_2O \quad = 2C_6H_{12}O_6$$
$$\text{Malt sugar} \qquad\qquad \text{Glucose}$$

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6$$
$$\text{Starch} \qquad\qquad \text{Glucose}$$

On the large scale glucose is made by the hydrolysis of potato starch with hydrochloric acid.
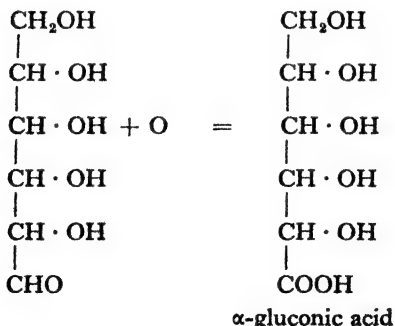
Properties.—Glucose is a wax-like solid mass which crystallizes with one molecule of water of crystallization. It is white when fresh, but soon turns yellow and becomes extremely hard. Anhydrous glucose melts at 146° C., but the hydrated form liquefies at 86° C. It is soluble in its own weight of water but is almost insoluble in absolute alcohol. It is the purest form of sugar, but is not so sweet as sucrose. It is dextro-rotatory, that is, its solution rotates the plane of polarization of polarized light to the right (p. 257). A 10 per cent solution turns the plane 52·5° to the right at 20° C. In symbols $\left[\alpha\right]_{D}^{20} = +52\cdot5$.

On fermentation with yeast it is converted into ethyl alcohol and carbon dioxide (p. 110).

The following reactions serve to illustrate additional properties of glucose, as well as to indicate its internal structure.
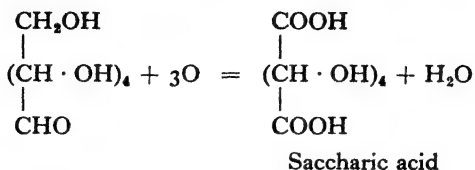
Reactions.—1. On oxidation:

(*a*) With chlorine or bromine water, glucose is converted into an acid containing the same number of carbon atoms (6), a property which shows it to be an aldehyde and not a ketone (p. 188):

$$
\begin{array}{ccc}
CH_2OH & & CH_2OH \\
| & & | \\
CH\cdot OH & & CH\cdot OH \\
| & & | \\
CH\cdot OH + O & = & CH\cdot OH \\
| & & | \\
CH\cdot OH & & CH\cdot OH \\
| & & | \\
CH\cdot OH & & CH\cdot OH \\
| & & | \\
CHO & & COOH
\end{array}
$$

<div align="center">α-gluconic acid</div>

(*b*) With powerful oxidizing agents such as nitric acid,

glucose is converted into saccharic acid; both the $-CH_2OH$ and $-CHO$ groups undergo oxidation:

$$
\begin{array}{ccc}
CH_2OH & & COOH \\
| & & | \\
(CH \cdot OH)_4 + 3O & = & (CH \cdot OH)_4 + H_2O \\
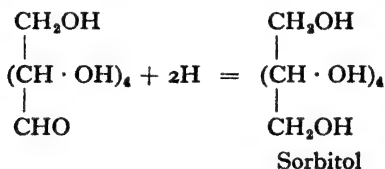| & & | \\
CHO & & COOH
\end{array}
$$

Saccharic acid

Saccharic acid is a very soluble deliquescent compound.

Further oxidation with concentrated nitric acid converts glucose into oxalic acid:

$$
C_6H_{12}O_6 + 9O = 3\left|\begin{array}{l} COOH \\ COOH \end{array}\right. + 3H_2O
$$

Glucose   Oxalic acid
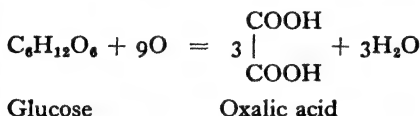
2. On reduction with sodium amalgam in aqueous solution glucose is converted into a primary alcohol, sorbitol; this is another proof of the aldehydic structure of glucose:
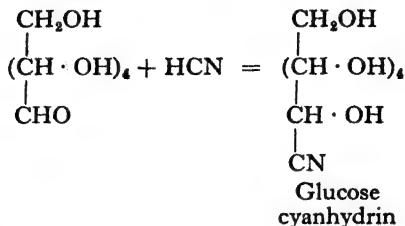
$$
\begin{array}{ccc}
CH_2OH & & CH_2OH \\
| & & | \\
(CH \cdot OH)_4 + 2H & = & (CH \cdot OH)_4 \\
| & & | \\
CHO & & CH_2OH
\end{array}
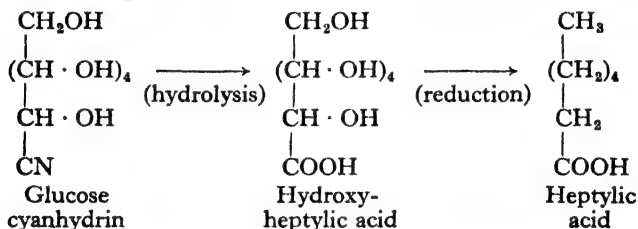$$

Sorbitol

3. Glucose is a strong reducing agent. It reduces

(a) Tollen's reagent, forming a silver mirror (cf. p. 526).
(b) Fehling's solution (p. 527), forming cuprous oxide.
(c) Gold and platinum from warm solutions of their salts.

Fehling's solution is used in the quantitative estimation of glucose, and of sucrose (after inversion) (p. 599).

4. It forms an additive compound with prussic acid:

$$
\begin{array}{ccc}
CH_2OH & & CH_2OH \\
| & & | \\
(CH \cdot OH)_4 + HCN & = & (CH \cdot OH)_4 \\
| & & | \\
CHO & & CH \cdot OH \\
& & | \\
& & CN \\
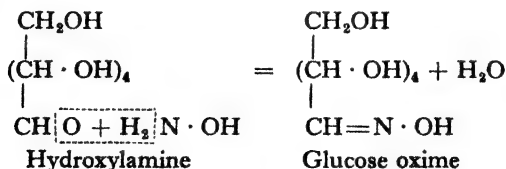& & \text{Glucose} \\
& & \text{cyanhydrin}
\end{array}
$$

On hydrolysis followed by reduction, glucose cyanhydrin is finally converted into a fatty acid, heptylic acid, which contains a straight chain of 6 carbon atoms terminated by a carboxyl group:

$$
\begin{array}{ccccc}
CH_2OH & & CH_2OH & & CH_3 \\
| & & | & & | \\
(CH \cdot OH)_4 & \xrightarrow{\text{(hydrolysis)}} & (CH \cdot OH)_4 & \xrightarrow{\text{(reduction)}} & (CH_2)_4 \\
| & & | & & | \\
CH \cdot OH & & CH \cdot OH & & CH_2 \\
| & & | & & | \\
CN & & COOH & & COOH \\
\text{Glucose} & & \text{Hydroxy-} & & \text{Heptylic} \\
\text{cyanhydrin} & & \text{heptylic acid} & & \text{acid}
\end{array}
$$

Glucose, therefore, is a straight chain compound with an aldehydic group at the end of the chain.

5. It reacts

(a) With hydroxylamine in alcoholic solution to form an **oxime**:

$$
\begin{array}{ccc}
CH_2OH & & CH_2OH \\
| & & | \\
(CH \cdot OH)_4 & = & (CH \cdot OH)_4 + H_2O \\
| & & | \\
CH\,\fbox{$O + H_2$}\,N \cdot OH & & CH{=}N \cdot OH \\
\text{Hydroxylamine} & & \text{Glucose oxime}
\end{array}
$$

. (b) With phenylhydrazine to form an **osazone.** The glucose first reacts with phenylhydrazine, forming glucose phenylhydrazone, which is then oxidized by a second molecule of phenylhydrazine to form the ketone known as

phenylhydrazone of glucosone. Finally, this ketone reacts with a third molecule of phenylhydrazine to form phenyl glucosazone. These reactions are represented as follows *:
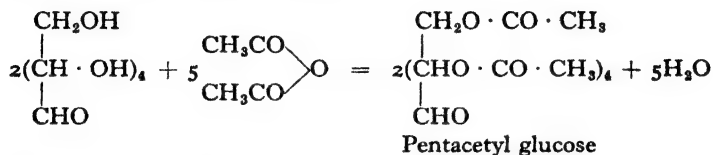
$$\begin{array}{c} CH_2OH \\ | \\ (CH \cdot OH)_4 \\ | \\ CH\overline{|O + H_2|}N \cdot NH \cdot C_6H_5 \\ \text{Phenylhydrazine} \end{array} = \begin{array}{c} CH_2OH \\ | \\ (CH \cdot OH)_4 \qquad + H_2O \\ | \\ CH : N \cdot NH \cdot C_6H_5 \\ \text{Glucose phenylhydrazone} \end{array}$$

$$\begin{array}{c} CH_2OH \\ | \\ (CH \cdot OH)_3 \\ | \\ CH \cdot O\overline{|H + H_2N|} \cdot NHC_6H_5 \\ | \\ CH : N \cdot NH \cdot C_6H_5 \end{array} = \begin{array}{c} CH_2OH \\ | \\ (CH \cdot OH)_3 \\ | \\ CO \quad + \quad NH_3 \quad + \quad C_6H_5NH_2 \\ | \qquad\qquad\qquad\qquad \text{Aniline} \\ CH : N \cdot NH \cdot C_6H_5 \\ \text{Phenylhydrazone of} \\ \text{glucosone} \end{array}$$

$$\begin{array}{c} CH_2OH \\ | \\ (CH \cdot OH)_3 \\ | \\ C\overline{|O + H_2|}N \cdot NH \cdot C_6H_5 \\ | \\ CH : N \cdot NH \cdot C_6H_5 \end{array} = \begin{array}{c} CH_2OH \\ | \\ (CH \cdot OH)_3 \\ | \qquad\qquad + H_2O \\ C : N \cdot NH \cdot C_6H_5 \\ | \\ CH : N \cdot NHC_6H_5 \\ \text{Phenyl glucosazone} \end{array}$$

These reactions with hydroxylamine and phenylhydrazine indicate that glucose is either an aldehyde or a ketone.

Experiment.—Make a solution of phenylhydrazine acetate by dissolving 2 gm. of phenylhydrazine in 2 c.c. of glacial acetic acid. Add 15 c.c. of water to this mixture and shake until clear. Dissolve about 1 gm. of glucose in 5–10 c.c. of water and add this solution to the phenylhydrazine acetate solution contained in a small carbon dioxide flask. Mix thoroughly and warm on the water bath for half an hour; yellow crystals of phenyl glucosazone are deposited. Filter, wash with cold water and dry. Take the melting-point of the osazone (204° C.).

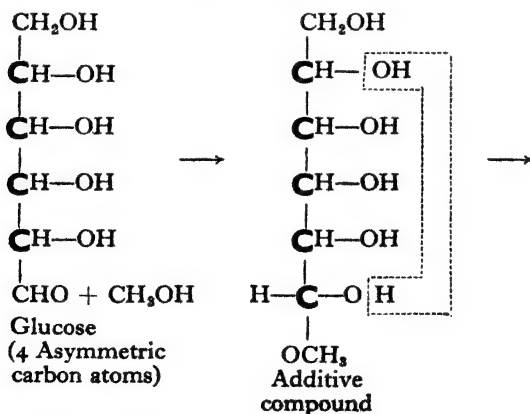* The sign : is frequently used to denote a double bond.

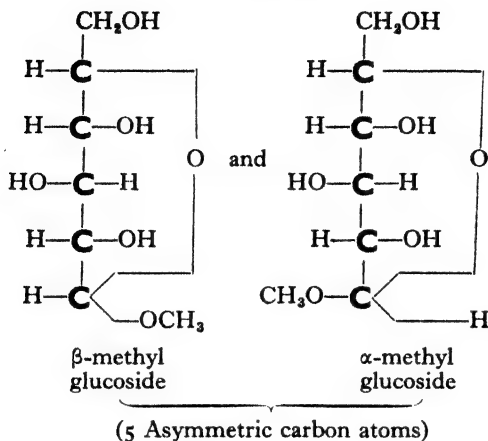A purer product is obtained by recrystallization from hot pyridine.

6. It forms a pentacetyl derivative when heated with acetic anhydride and anhydrous sodium acetate. This derivative can be hydrolysed to acetic acid and glucose when boiled with acids and alkalis:

$$
\begin{array}{l}
CH_2OH \\
\;|\\
2(CH \cdot OH)_4 \;+\; 5 \;\; {}^{CH_3CO}_{CH_3CO}\!\!>\!\!O \;=\; 2(CHO \cdot CO \cdot CH_3)_4 \;+\; 5H_2O \\
\;|\\
CHO
\end{array}
$$

$$
\begin{array}{l}
CH_2O \cdot CO \cdot CH_3 \\
\;|\\
\;|\\
CHO
\end{array}
$$
Pentacetyl glucose

This reaction indicates that glucose contains five hydroxyl —OH groups in the molecule.

7. It reacts with alcohols to form **glucosides.** Methyl glucoside is formed by dissolving glucose in cold methyl alcohol saturated with dry hydrogen chloride, and allowing to stand for several hours. Apparently the aldehyde group combines with the alcohol to form an unstable compound which loses a molecule of water to form two stereo-isomeric glucosides known as α-methyl glucoside and β-methyl glucoside, which have a cyclic structure:

$$
\begin{array}{l}
CH_2OH \\
\;|\\
CH{-}OH \\
\;|\\
CH{-}OH \\
\;|\\
CH{-}OH \\
\;|\\
CH{-}OH \\
\;|\\
CHO + CH_3OH
\end{array}
\longrightarrow
\begin{array}{l}
CH_2OH \\
\;|\\
CH{-}\boxed{OH} \\
\;|\\
CH{-}OH \\
\;|\\
CH{-}OH \\
\;|\\
CH{-}OH \\
\;|\\
H{-}C{-}O\,\boxed{H} \\
\;|\\
OCH_3
\end{array}
\longrightarrow
$$

Glucose
(4 Asymmetric carbon atoms)

Additive compound

$$\begin{array}{ccc}
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\
\text{H}-\text{C} & & \text{H}-\text{C} \\
\text{H}-\text{C}-\text{OH} & & \text{H}-\text{C}-\text{OH} \\
\text{HO}-\text{C}-\text{H} \quad \text{O} \quad \text{and} & & \text{HO}-\text{C}-\text{H} \quad \text{O} \\
\text{H}-\text{C}-\text{OH} & & \text{H}-\text{C}-\text{OH} \\
\text{H}-\text{C}\diagdown & & \text{CH}_3\text{O}-\text{C}\diagdown \\
\text{OCH}_3 & & \text{H}
\end{array}$$

β-methyl   α-methyl
glucoside   glucoside

(5 Asymmetric carbon atoms)

Natural Glucosides include amygdalin, $C_{20}H_{27}O_{11}N$, found in bitter almonds; salicin, $C_{13}H_{18}O_7$, found in willow bark and in poplars, used in medicine as a remedy for rheumatism and malarial fever, and as a febrifuge; sinigrin, $C_{10}H_{16}O_9NS_2K$, found in black mustard seed; phloridzin, $C_{21}H_{24}O_{10}$, found in the root bark of fruit trees, used to produce *glycosuria* (a condition in which sugar appears in the urine) when injected subcutaneously; indican, $C_{14}H_{17}O_6N$, found in the indigo plant.

Uses.—Glucose is used in confectionery, preserves, syrups, jams, jellies, &c.; in chewing gum and chewing tobacco and in the manufacture of glassy sweets; in sizes for textiles and soaps and as a substitute for malt in brewing. It is a valuable food material. Glucose-D is used in cases of acidosis; it contains pure glucose (98%), ostelin vitamin D, and a compound of calcium and phosphorus (2%).

Tests for Glucose are given on p. 534.

Fructose, Fruit Sugar, or **Lævulose,** $C_6H_{12}O_6$, is very widely distributed in plants, in ripe fruits, and in honey and is also produced by the hydrolysis of certain

starch-like compounds, such as inulin, which occurs in dahlia tubers. The name lævulose arose from its lævo-rotation, but since a dextro-rotatory fruit sugar is known, the natural sugar is now called fructose.

Formation.

1. From glucose by treatment with phenylhydrazine. The phenyl glucosazone thus formed is converted into glucosone on hydrolysis with hydrochloric acid. Finally, the glucosone yields fructose on reduction.

$$
\begin{array}{l}
CH_2OH \\
| \\
(CH \cdot OH)_3 \\
| \\
C : N \cdot NHC_6H_5 \\
| \\
CH : N \cdot NHC_6H_5 \\
\text{Phenyl glucosazone}
\end{array}
\; + 2HOH = \;
\begin{array}{l}
CH_2 \cdot OH \\
| \\
(CH \cdot OH)_3 \\
| \\
CO \\
| \\
CHO \\
\text{Glucosone}
\end{array}
\; + 2NH_2 \cdot NH \cdot C_6H_5 \\
\text{Phenylhydrazine}
$$

$$
\begin{array}{l}
CH_2OH \\
| \\
(CH \cdot OH)_3 \\
| \\
CO \\
| \\
CHO
\end{array}
\; + 2H \; = \;
\begin{array}{l}
CH_2OH \\
| \\
(CH \cdot OH)_3 \\
| \\
CO \\
| \\
CH_2OH \\
\text{Fructose}
\end{array}
$$
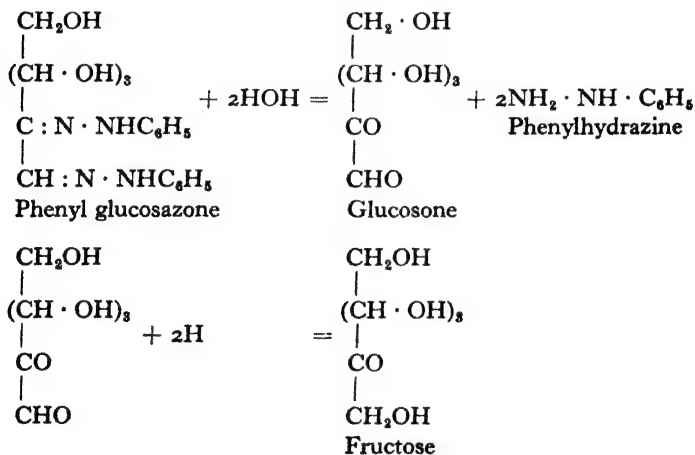
This method of formation indicates that fructose is a ketone and that it is closely related stereo-chemically to glucose, and for this reason, although ordinary fructose is lævo-rotatory, it is known as *d*-fructose.

2. From cane sugar by hydrolysis with dilute sulphuric acid. The excess of acid is removed with barium carbonate, which is precipitated as barium sulphate and filtered off. The filtrate is then concentrated and treated with milk of lime; slightly soluble calcium fructosate is deposited, filtered

off, and suspended in water; the calcium is then precipitated as calcium carbonate by bubbling carbon dioxide through the suspension:

$$C_6H_{11}O_6Ca(OH) + CO_2 = C_6H_{12}O_6 + CaCO_3$$
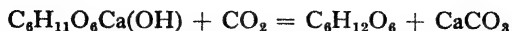
The calcium carbonate is removed by filtration. The filtrate is then concentrated at 80° C. and allowed to crystallize, the crystallization being hastened by the introduction of a crystal of fructose. The crystals are purified by recrystallization from alcohol. Calcium compounds of the type mentioned above are extensively used in the purification of sugars (p. 363).

3. From inulin by hydrolysis with sulphuric acid:

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6$$
Inulin   Fructose
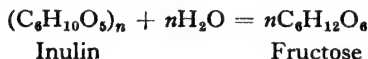
The excess of acid is removed and crystallization is conducted as described under 2.

Properties.—Fructose crystallizes in rhombic prisms, m. pt. 95° C. It is more soluble in water and in alcohol than glucose is. It is said to be one and a half times as sweet as cane sugar. Fructose obtained from inulin is used by diabetics, since it can be assimilated by them, whereas cane sugar and glucose are excreted in the free state. Fructose may be fermented by yeast, but less rapidly than glucose, yielding the same products (p. 235). Fructose is lævo-rotatory; its solution rotates the plane of polarization 92° to the left: $\left[\alpha\right]_D^{20} = -92°$.

The following reactions serve to illustrate additional properties of fructose as well as to indicate its internal structure; they should be compared with the corresponding reactions of glucose.

Reactions.—1. On oxidation:

(*a*) With bromine water or nitric acid fructose is converted

into glycollic, oxalic and mesotartaric acids, but no saccharic acid is formed (contrast glucose):

$$
\begin{array}{l}
CH_2OH \\
| \\
CH \cdot OH \\
| \\
CH \cdot OH + 2O_2 \\
| \\
CH \cdot OH \\
| \\
CO \\
| \\
CH_2OH
\end{array}
\quad = \quad
\begin{array}{l}
CH_2OH \\
| \\
COOH \\
\text{Glycollic} \\
\text{acid}
\end{array}
\quad + \quad
\begin{array}{l}
COOH \\
| \\
CH \cdot OH \\
| \\
CH \cdot OH + H_2O \\
| \\
COOH \\
\text{Mesotartaric acid}
\end{array}
$$
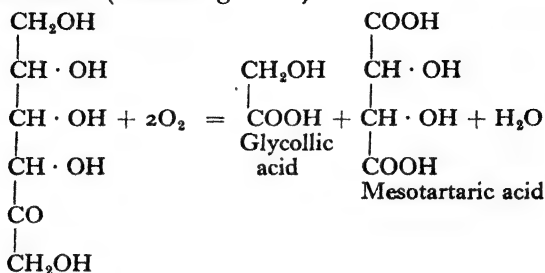
The oxalic acid results from the oxidation of some of the glycollic acid.

(*b*) With mercuric oxide in aqueous solution fructose is converted into glycollic and trihydroxy-butyric acids:

$$
\begin{array}{l}
CH_2OH \\
| \\
(CH \cdot OH)_3 \\
| \\
CO \\
| \\
CH_2OH \\
\text{Fructose}
\end{array}
\quad + O_2 = \quad
\begin{array}{l}
CH_2OH \\
| \\
COOH \\
\text{Glycollic} \\
\text{acid}
\end{array}
\quad + \quad
\begin{array}{l}
CH_2OH \\
| \\
CH \cdot OH \\
| \\
CH \cdot OH \\
| \\
COOH \\
\text{Trihydroxy-} \\
\text{butyric acid}
\end{array}
$$
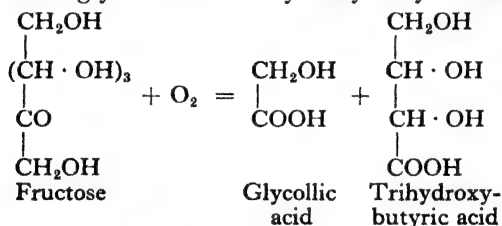
The formation of these products shows that fructose is a ketose having the above structure and not an aldehyde, as it does not yield an acid containing the same number of carbon atoms as itself.

2. On reduction fructose yields equal amounts of *d*-mannitol and *d*-sorbitol (contrast glucose):

$$
2 \;
\begin{array}{l}
CH_2OH \\
| \\
(CH \cdot OH)_3 \\
| \\
CO \\
| \\
CH_2OH
\end{array}
\quad + 4H = \quad
\begin{array}{l}
CH_2OH \\
| \\
(CH \cdot OH)_3 \\
| \\
H-C-OH \\
| \\
CH_2OH \\
\textit{d-mannitol}
\end{array}
\quad + \quad
\begin{array}{l}
CH_2OH \\
| \\
(CH \cdot OH)_2 \\
| \\
OH-C-H \\
| \\
CH_2OH \\
\textit{d-sorbitol}
\end{array}
$$
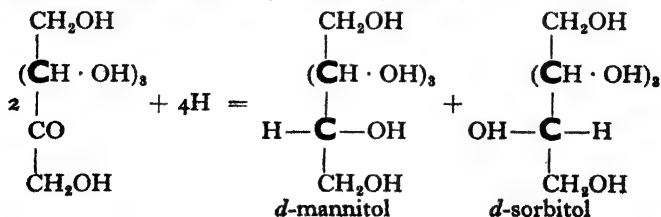
These compounds are stereo-isomers containing asymmetric carbon atoms (shown by heavy type) and secondary alcoholic groups, which indicate that fructose contains a ketone —CO group.

3. It is a strong reducing agent. It reduces Tollen's reagent and Fehling's solution more rapidly than but not to the same extent as glucose. This is due to the presence of the easily oxidizable —CO · CH$_2$OH group. All ketonic alcohols containing this group are strong reducing agents.

4. It forms an additive compound with prussic acid:

$$
\begin{array}{ccc}
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\
| & & | \\
(\text{CHOH})_3 & & (\text{CH} \cdot \text{OH})_3 \\
| & & | \quad\diagup\text{OH} \\
\text{CO} & +\ \text{HCN}\ = & \text{C}\diagdown \\
| & & | \quad\diagdown\text{CN} \\
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH}
\end{array}
$$

<div align="center">Fructose cyanhydrin</div>
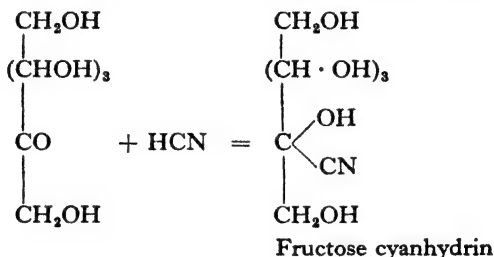
Fructose cyanhydrin on hydrolysis is converted into a hydroxy-acid, and when this compound is reduced with hydriodic acid and a little red phosphorus, methyl butyl acetic acid is formed:

$$
\begin{array}{ccccc}
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} & & \text{CH}_3 \\
| & & | & & | \\
(\text{CH} \cdot \text{OH})_3 & \text{hydrolysis} & (\text{CH} \cdot \text{OH})_3 & \text{reduction (HI)} & (\text{CH}_2)_3 \\
| \quad\diagup\text{OH} & \longrightarrow & | \quad\diagup\text{OH} & \longrightarrow & | \\
\text{C}\diagdown & & \text{C}\diagdown & & \text{CH} \cdot \text{COOH} \\
| \quad\diagdown\text{CN} & & | \quad\diagdown\text{COOH} & & | \\
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} & & \text{CH}_3 \\
& & \text{Hydroxy-acid} & & \text{Methyl butyl} \\
& & & & \text{acetic acid}
\end{array}
$$
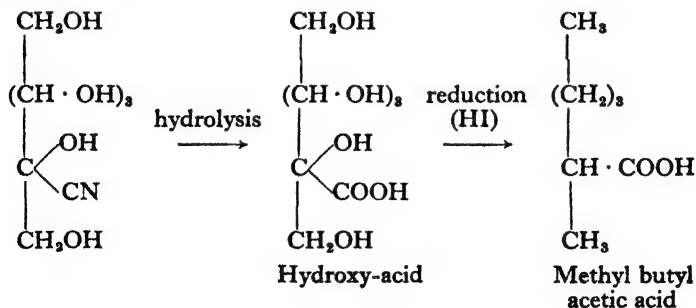
These reactions indicate that fructose is a hydroxy-ketone

in which the ketone group is attached to one of the end carbon atoms.

5. It reacts:

(a) With hydroxylamine in alcoholic solution to form an oxime isomeric with that obtained from glucose:

$$
\begin{array}{ccc}
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\
| & & | \\
(\text{CH}\cdot\text{OH})_3 & & (\text{CH}\cdot\text{OH})_3 \\
| & = & | \\
\text{C}\,\boxed{\text{O}\qquad +\,\text{H}_2}\,\text{NOH} & & \text{C}:\text{N}\cdot\text{OH} \\
| & & | \\
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH}
\end{array}\; +\,\text{H}_2\text{O}
$$

<center>Fructose oxime</center>
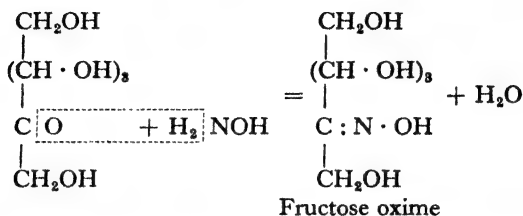
(b) With phenylhydrazine to form the same osazone as that obtained from glucose:

$$
\begin{array}{ccc}
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\
| & & | \\
(\text{CH}\cdot\text{OH})_3 & & (\text{CH}\cdot\text{OH})_3 \\
| & = & | \\
\text{C}\,\boxed{\text{O} + \text{H}_2}\,\text{N}\cdot\text{NHC}_6\text{H}_5 & & \text{C}:\text{N}\cdot\text{NHC}_6\text{H}_5 \\
| & & | \\
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH}
\end{array}\; +\,\text{H}_2\text{O}
$$

<center>Fructose phenylhydrazone</center>

$$
\begin{array}{ccc}
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\
| & & | \\
(\text{CH}\cdot\text{OH})_3 & & (\text{CH}\cdot\text{OH})_3 \\
| & = & | \\
\text{C}:\text{N}\cdot\text{NHC}_6\text{H}_5 & & \text{C}:\text{N}\cdot\text{NHC}_6\text{H}_5 \\
| & & | \\
\text{CH}_2\text{O}\,\boxed{\text{H} + \text{NH}_2}\,\text{NHC}_6\text{H}_5 & & \text{CHO}
\end{array}\; +\,\text{C}_6\text{H}_5\cdot\text{NH}_2 + \text{NH}_3
$$

$$
\begin{array}{ccc}
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\
| & & | \\
(\text{CH}\cdot\text{OH})_3 & & (\text{CH}\cdot\text{OH})_3 \\
| & = & | \\
\text{C}:\text{N}\cdot\text{NHC}_6\text{H}_5 & & \text{C}:\text{N}\cdot\text{NHC}_6\text{H}_5 \\
| & & | \\
\text{CH}\,\boxed{\text{O} + \text{H}_2}\,\text{N}\cdot\text{NHC}_6\text{H}_5 & & \text{CH}\cdot\text{N}\cdot\text{NHC}_6\text{H}_5
\end{array}\; +\,\text{H}_2\text{O}
$$

<center>Fructosazone</center>
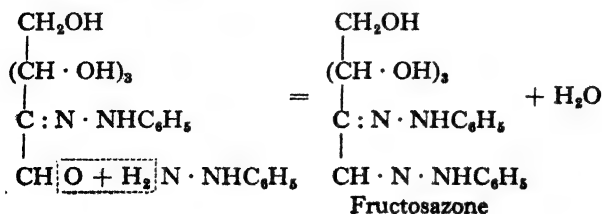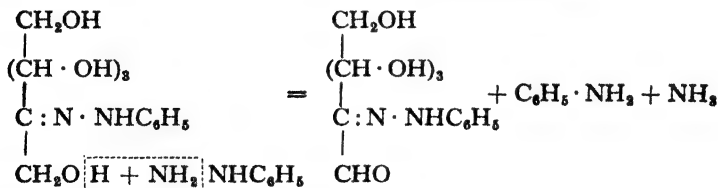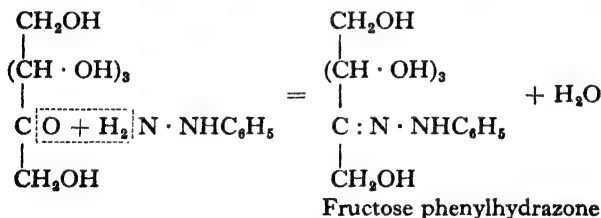
6. It forms a pentacetyl derivative similar to that of glucose, and therefore contains five hydroxyl groups in the molecule.

Constitution of Sugars.

The reactions described under glucose and fructose serve to illustrate the constitution of the sugars.

1. The nature of the sugar (whether aldose or ketose) is shown by the behaviour on oxidation and reduction and by the reactions with hydroxylamine, phenylhydrazine, &c.

2. The nature of the chain is investigated by the formation of cyanhydrins, followed by the conversion of these products by hydrolysis into polyhydric acids.

3. The number of hydroxyl groups is found by converting them into pentacetyl or a lesser or greater number of acetyl —$O \cdot COCH_3$ groups.

The following is an example of the determination and calculation of the number of hydroxyl groups in a sugar. A known weight of the acetyl compound is hydrolysed with an aqueous solution of benzene sulphonic acid, $C_6H_5 \cdot SO_3H$, which liberates the acetic acid. This is driven off in a current of steam, condensed, and estimated by titration with standard baryta water, using phenolphthalein as indicator.

Example.

Molecular weight of sugar   = 342.
Weight of acetyl compound taken = 0·565 gm.
Weight of acetic acid liberated = 0·400 gm.

Now the molecular weight of acetic acid (60) corresponds to one hydroxyl group —OH of molecular weight 17.

∴ the weight of hydroxyl equivalent to 0·4 gm. of acetic acid

$$= \frac{0 \cdot 4}{60} \times 17 = 0 \cdot 1133 \text{ gm.}$$

Since OH $\equiv$ O $\cdot$ COCH$_3$ $\equiv$ CH$_3$COOH
17 gm. hydroxyl $\equiv$ 59 gm. acetyl $\equiv$ 60 gm. acetic acid.

Then 60 gm. of acetic acid correspond to an increase in the weight of the sugar of 42 gm. (59 — 17) in the formation of the acetyl compound.

$\therefore$ 0·4 gm. corresponds to an increase of $\dfrac{42}{60} \times 0\cdot4 = 0\cdot28$ gm.

$\therefore$ the original weight of the sugar $= 0\cdot565 - 0\cdot28 = 0\cdot285$ gm. i.e. 0·285 gm. of sugar contains 0·1133 gm. of hydroxyl

$\therefore$ 342 gm. of sugar contain $\dfrac{0\cdot1133}{0\cdot285} \times 342$ gm. of hydroxyl.

$\therefore$ Number of OH groups in the sugar $= \dfrac{0\cdot1133}{0\cdot285} \times \dfrac{342}{17}$

$$= 7\cdot99, \text{ i.e. } 8 \text{ (cane sugar, \&c.)}.$$

Complex Sugars

These include the Disaccharoses and Trisaccharoses.

Sucrose or **Cane Sugar,** $C_{12}H_{22}O_{11}$, occurs in large quantities in nature in the sugar cane (up to 20 per cent) in the sugar beet (up to 17 per cent), and in smaller quantities in various fruits and plants such as the sugar maple, maize and sorghum.

Cane sugar is produced almost entirely from the sugar cane and the sugar beet. The processes of extraction are very similar.

The Cane-sugar Industry.—The sugar cane is cut up and crushed in roller presses to express the juice. The cold juice is heated and cream of lime run in to neutralize any acid which might hydrolyse the sugar, as well as to combine with some of the impurities and to coagulate the vegetable proteins which might undergo fermentation. These impurities are allowed to settle and the clear juice is run off. The slight excess of lime present is precipitated as calcium carbonate by bubbling in carbon dioxide, and the precipitate is removed by passing the solution through filter presses. The clear juice is then concentrated in

steam-heated vacuum evaporators to a syrup known as *massecuite*. When this is cold, crystals of cane sugar are deposited, and are separated from the mother liquor or cane sugar molasses by centrifugal machines.

Cane sugar molasses has a pleasant taste and is usually treated further in order to extract more sugar, as described below. Some of the molasses, however, is used as a table syrup and in baking, or fermented to make alcohol.

The Beet-sugar Industry.—The juice of sugar beet, is extracted by the diffusion process. This consists in first washing the beets with water to free them from earthy impurities, then cutting them up into thin chips and placing them in large vessels called diffusers. Here the beets are treated with hot water; the cell walls of the beets permit the sugar to diffuse into the water but retain the non-diffusable colloidal substances. This separation may be regarded as a process of dialysis. The " sweet water " then passes through a battery of diffusers containing sugar beet and in so doing abstracts more sugar and increases in concentration. The sugar juice is then treated with cream of lime and carbon dioxide as described under cane sugar. The purified juice is sometimes subjected to the *sulphitation* process, that is, it is treated with sulphur dioxide to bleach it and to precipitate any calcium left as calcium sulphite. This process of refining is not used in this country.

Beet sugar molasses has an unpleasant taste, and hence is not used as a foodstuff. It is sometimes used as a cattle food, and also for making alcohol.

Molasses Extraction.—The molasses obtained from these two processes may contain up to 50 per cent of sucrose which does not crystallize. The sugar is recovered by treating the molasses with a hot solution of cream of lime, which precipitates the sugar as calcium sucrosate, $C_{12}H_{22}O_{11} \cdot 3CaO$.

This precipitate is filtered off, washed, suspended in water and decomposed by carbon dioxide, which precipitates calcium carbonate, leaving the sugar in solution. The liquid is then filtered; if the juice is slightly discoloured it is decolorized by being made to pass through bone charcoal contained in tall vertical cylindrical tanks. Finally the juice is concentrated to a syrup and treated as described above.

The decolorizing value of the charcoal diminishes in time. The charcoal is then regenerated by washing with water and transferring to revivification kilns heated externally. This dries the charcoal and burns off the organic colouring matter. The charcoal is passed over a series of sieves to eliminate dust and returned to the decolorizing tanks.

Properties.—Cane sugar forms prismatic crystals. It is soluble in water but sparingly soluble in alcohol. It melts at 160° to 161° C. and then solidifies to an amorphous hard glass-like mass called *barley sugar.* At about 200° to 210° C. sucrose loses water, turns brown, and forms *caramel*, which is used in confectionery and for colouring spirits, soups, &c. Heated still further, sucrose carbonizes, forming sugar charcoal, and gives off gases containing acetic acid, acetone, and other products.

Sugar candy is formed by allowing cane sugar to deposit slowly on threads suspended in its solution.

Cane sugar is dextro-rotatory: $\left[a\right]_{D}^{20} = +66 \cdot 5$ in a 10 per cent aqueous solution.

Reactions.—1. It is hydrolysed by dilute mineral acids or by the enzyme *invertase* (in yeast) into equal amounts of glucose and fructose, and since the fructose is more strongly lævo-rotatory $\left(\left[a\right]_{D}^{20} = -92\right)$ than the glucose is dextro-rotatory $\left(\left[a\right]_{D}^{20} = +52 \cdot 5°\right)$ the mixture is lævo-rotatory. For

this reason it is called *invert sugar*, and the term *inversion* is used for the hydrolysis of the disaccharoses into monosaccharoses:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
(yeast)   Glucose   Fructose
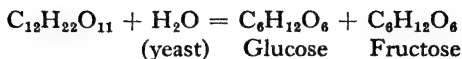
2. It is oxidized by strong nitric acid to form oxalic acid (p. 280).

3. It is converted by strong hydrochloric acid into levulinic acid, $CH_3CO(CH_2)_2 COOH$.

4. Strong sulphuric acid decomposes and finally chars it with evolution of carbon dioxide and sulphur dioxide.

5. It forms saccharosates or sucrosates with certain metals, e.g.:

$$C_{12}H_{22}O_{11} \cdot 3CaO; \qquad C_{12}H_{22}O_{11} \cdot nSrO,$$

where $n = 1, 2$ or 3.

6. It does not undergo fermentation directly, but only after hydrolysis.

7. It is not acted on by alkalis.

Saccharimetry is the method of estimating:

(*a*) the percentage of sucrose present in sugar juice, molasses, &c.,

(*b*) the concentration of a sugar solution, by determining the optical rotation in a special type of polarimeter known as a saccharimeter.

Constitution of Cane Sugar.✕

Cane sugar does not reduce Fehling's solution (cf. p. 351), nor does it react with hydroxylamine or phenylhydrazine; hence it is neither an aldehyde nor a ketone. Glucose and fructose have been made to combine with elimination of a molecule of water to form cane sugar as a condensation product. It is assumed that these two hexoses are combined in such a way that the aldehyde group of glucose is

linked with the ketone group of fructose, a molecule of water being eliminated from two hydroxyl groups:

$$
\begin{array}{llll}
CH_2OH & CH_2OH & CH_2OH & CH_2OH \\
| & | & | & | \\
CH \cdot O\;\boxed{H\;OH}\;\;—CH & —CH & CH\;\;——\; \\
| & | & | & | \\
CH \cdot OH & CH \cdot OH & CH \cdot OH & CH \cdot OH \\
| \;\;\;\;\;+ & | \;\;\;\;\;= & | & | \;\;\;\;\;\; O \\
CH \cdot OH & CH \cdot OH & CH \cdot OH & CH \cdot OH \\
| & | & O\;\;| & | \\
CH \cdot OH & CO & CH \cdot OH & C\;\;——— \\
| & | & | & | \\
CHO & CH_2OH & —CH——— & CH_2OH \\
\text{Glucose} & \text{Fructose} & \text{Glucose} & \text{Fructose} \\
 & & \text{residue} & \text{residue}
\end{array}
$$

Sucrose

or

$$
HO \cdot HC \begin{array}{l} \diagup CH(OH) \cdot CH(OH) \diagdown \\ \diagdown CH ——— O \diagup \end{array} CH — O — C \begin{array}{l} \diagup CH(OH) \cdot CH(OH) \\ \diagdown O ——— CH \cdot CH_2(OH) \end{array}
$$
$$
\;\;\;\;\; | \; |
$$
$$
CH_2OH \; CH_2OH
$$

Glucose residue   Fructose residue
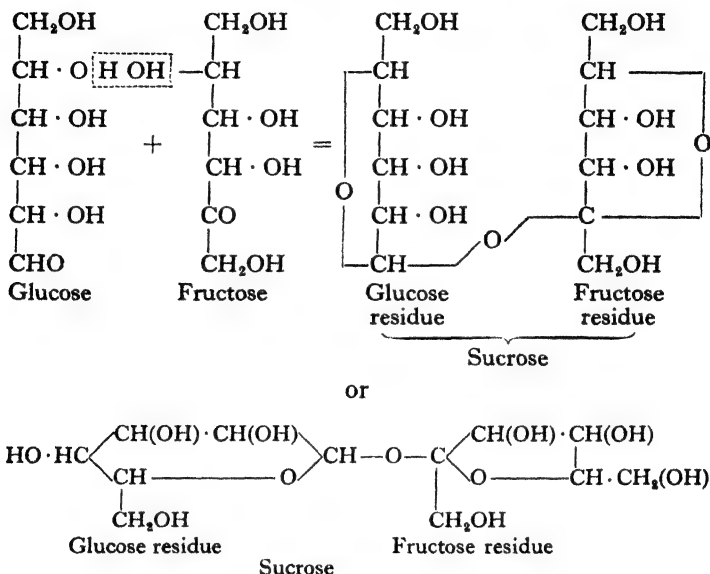
Sucrose

In all probability the formation of sucrose is due to the tendency of the carbonyl —CO— group of glucose and fructose to link itself with one of the —CHOH groups and so form a closed chain or cyclic compound, an assumption justified by the fact that sucrose contains two closed-chain groups derived from the glucose and fructose residues respectively.

This structure accounts for the following facts:

(a) The formation of an octacetyl derivative (m. pt. 67°C.), and an octamethyl ether;

(b) the absence of all reducing properties;

(c) the readiness with which it can be hydrolysed, since the two hexoses are united by means of an atom of oxygen;

(d) the non-formation of an osazone.

Maltose or **Malt Sugar**, $C_{12}H_{22}O_{11}$, is formed by the action of the ferment *diastase* on starch. It is the chief constituent sugar in malt, from which it is extracted; hence its name. It crystallizes in fine needles; it is soluble in water and its solution is dextro-rotatory $\left(\left[\alpha\right]_D^{20} = +137°\right)$. On hydrolysis with dilute sulphuric acid it is converted into glucose:

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$
$$\text{Maltose} \qquad\qquad \text{Glucose}$$
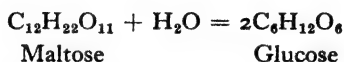
It reduces Fehling's solution and reacts with phenylhydrazine to form maltosazone (m. pt. 206° C.). It is therefore an aldehyde. It also has eight hydroxyl groups (forms an octacetyl derivative).

Lactose or **Milk Sugar**, $C_{12}H_{22}O_{11} \cdot H_2O$, is present in the milk of mammals to the extent of 5 to 6 per cent. The average composition of cow's milk is

Water	=	87·35
Milk sugar	=	4·70
Proteins { Casein	=	3·00
Albumin	=	0·40
Fat (butter)	=	3·74
Ash (calcium phosphate, &c.)	=	0·81
		100·00

Specific gravity (average) = 1·0315

Lactose is a white crystalline solid; on heating to 130° C. it loses its water of crystallization. It is dextro-rotatory $\left(\left[\alpha\right]_D^{20} = +52\cdot5°\right)$. It reduces both Tollen's reagent and Fehling's solution and reacts with phenylhydrazine to form lactosazone (m. pt. 200° C.). It is therefore an aldose. On hydrolysis with dilute acids, or by the enzyme *lactase* found

in the intestine of the calf, it yields one molecule of glucose and one molecule of galactose, a stereo-isomer of glucose:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
Lactose   Glucose   Galactose
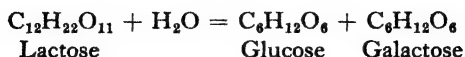
It gives an octacetyl derivative with acetic anhydride. On oxidation it yields an acid, lacto-bionic acid, containing the same number of carbon atoms. These reactions confirm the aldehydic character of lactose.

Lactose is used as a food and in pharmacy.

Polyoses

The complex carbohydrates have the general formula

$$(C_6H_{10}O_5)_n,$$

but little is known of the actual structure of the molecule.

Starch is found in the reserve food of plants. The chief sources of starch are the potato, rice, wheat, maize, &c. Starch is found as white grains in the plant cell; each plant forms its starch in granules which have a characteristic appearance, either round, elliptical or angular, under the microscope (fig. 38). By this means the source of the starch may be determined.

When boiled with water, starch grains burst, and a portion enters into solution, forming starch paste. The soluble portion is termed *granulose*, the insoluble portion *starch cellulose*. *Soluble starch* is formed by boiling starch with dilute acids under pressure or allowing it to remain in contact with cold concentrated hydrochloric acid. A characteristic test for starch is the formation of an intense blue colour with a trace of iodine.

Starch can be hydrolysed by:

(*a*) Hot mineral acids to form dextrin and maltose and finally glucose;
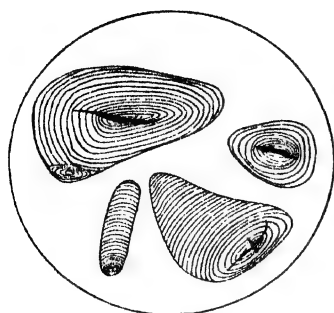
Sago Starch
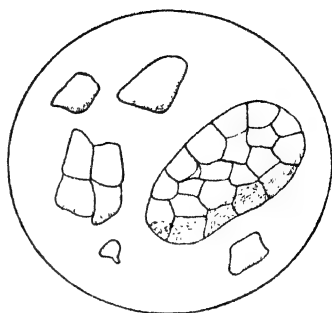
Rice Starch
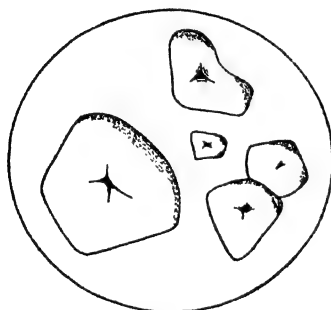
Maize Starch
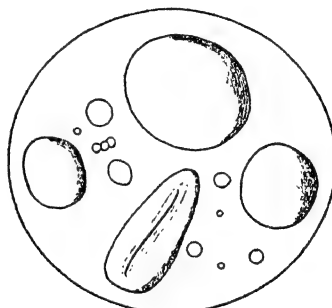
Wheat Starch

Potato Starch
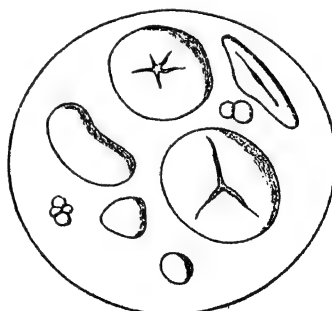
Rye Starch

Fig, 38.—Microscopic Appearance of Starch

(*b*) various enzymes such as *diastase* (in malt), *ptyalin* (in the saliva) to form dextrin and maltose;

(*c*) enzymes in the stomach and intestines to form maltose and glucose.

Dextrin or **Starch Gum,** $(C_6H_{10}O_5)_n$, is the name given to the whole class of gummy substances. They are used as adhesives for postage stamps, envelopes, &c.

Dextrin is made by gently heating starch to about 190° C., or by hydrolysing starch either with dilute hydrochloric acid or by the enzyme diastase. In addition to dextrin, compounds known as amyloïns are formed at the same time. The amyloïns are compounds of dextrin and maltose.

Glycogen or **Animal Starch,** $(C_6H_{10}O_5)$, is abundant in the liver of mammals. It is a reserve material or food in animals. It is converted into glucose by the liver or by the action of dilute acids. It is distinguished from plant starch by the wine-red coloration it gives with iodine. When pure it is a white and tasteless powder.

Cellulose, $(C_6H_{10}O_5)_n$, is the chief constituent of the cell walls of plants. It is used in many industries; as wood pulp in paper manufacture; as flax fibres for linen; as cotton for cotton goods; when nitrated, for explosives, photographic films, celluloid; and in the manufacture of artificial silk and " cellophane ".

Artificial silk is made by dissolving cellulose in Schweitzer's reagent (ammoniacal copper hydroxide) and forcing the solution through fine holes into dilute mineral acids, when fine threads which can be spun are obtained (cuprammonium silk). This, however, has been largely superseded by silk made from viscose (see p. 371).

Cellophane is made from the finest grade of Canadian wood pulp (spruce). The wood pulp, delivered in sheets, is first placed in a press and steeped in a solution of caustic soda and shredded. The alkali cellulose is then mixed

with carbon disulphide in rotating barrels, and is changed into orange cellulose xanthate.

$$(C_6H_{10}O_5)_n + nNaOH = nC_6H_9O_4 \cdot ONa + nH_2O,$$

$$C_6H_9O_4 \cdot ONa + CS_2 = CS \begin{cases} O \cdot C_6H_9O_4 \\ S \cdot Na \cdot \end{cases}$$

Cellulose xanthate
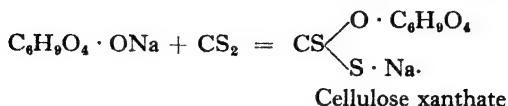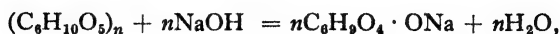
This compound is then mixed with more caustic soda, which converts it into an orange-coloured liquid called *viscose*. The viscose solution is allowed to stand for a period and is then forced under pressure through a narrow slit into an acid bath, where it coagulates and forms a continuous film of material of the required thickness. The film is then washed and bleached and dipped into a bath containing glycerol, which increases the pliability of the film. Finally the film is dried over heated rollers and emerges as " cellophane ", a transparent cellulose material. It is used mainly as a transparent dust-proof wrapping, also for bandages and hats, and as an insulator for electric wires.

The word " cellophane " is derived from cellulose, indicating its parent material and the Greek φανερός (*phaneros*), clear or transparent.

Parchment paper is made by the action of 80 per cent sulphuric acid on unsized paper for 15 to 20 seconds. The pores of the paper become filled with a gelatinous decomposition product of cellulose, probably $C_6H_7O_5(OH)(HSO_4)_2$, which makes it tougher and less porous. Cold concentrated sulphuric acid dissolves cellulose; on subsequent dilution and boiling, hydrolysis takes place, and glucose is formed, which is employed in beer manufacture and for cheap confectionery.

" Willesden " fabric is made by passing vegetable textiles, e.g. cotton, through a solution of cellulose in cuprammonium hydroxide; gelatinized cellulose containing copper

oxide is deposited in the pores of the fabric, rendering the fabric waterproof, rotproof and mildewproof, as well as colouring it green.

Cellulose contains three hydroxyl groups in each of its $C_6H_{10}O_5$ units, which can be acted upon to form mono-, di-, or tri-nitrates. These are cellulose esters.

Mononitrocellulose, $C_6H_7O_2(OH)_2NO_3$, and
Dinitrocellulose, $C_6H_7O_2(OH)(NO_3)_2$,

are known as pyroxylin, and dissolve in a mixture of ether and alcohol to form *collodion*, which is employed in the preparation of

(*a*) films by the evaporation of the volatile products,
(*b*) celluloid by mixing with camphor and evaporating.

Trinitrocellulose, $C_6H_7O_2(NO_3)_3$,

is known as gun-cotton and is used as an explosive.

Other cellulose esters which are important commercially include cellulose acetates, used as " dopes " for aeroplane wings and in the manufacture of artificial silk (acetate silk), and cellulose formates, used in making non-inflammable cinematograph films. Cellulose gives a brown colour with iodine and a blue colour with Schulze's solution (a zinc chloride solution containing iodine and potassium iodide).

Formation of Carbohydrates in Plants. This is thought to be due to the production of formaldehyde from carbon dioxide and water by the green leaves of plants in the presence of sunlight:

$$CO_2 + H_2O = H \cdot CHO + O_2$$
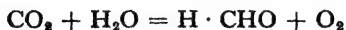
The formaldehyde in aqueous solution can be polymerized to a mixture of hexoses (cf. p. 164):

$$6H \cdot CHO = C_6H_{12}O_6 \text{ (fruit sugar, \&c.)}$$

and these again are converted into complex polyoses:

$$2C_6H_{12}O_6 = C_{12}H_{22}O_{11} + H_2O$$
Cane sugar,
&c.
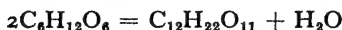
$$n \cdot C_{12}H_{22}O_{11} = (C_{12}H_{20}O_{10})_n + nH_2O$$
Starches,
Celluloses, &c.

This is known as the Formaldehyde Hypothesis of Photochemical Synthesis. For further information the student should consult textbooks on bio-chemistry.

Note.—The structural formulæ given in this chapter for glucose and fructose are not entirely correct. They are given to simplify matters for the student. The actual configurations of *d*-glucose and of *d*-fructose according to E. Fischer may be represented as follows:

```
        CH2OH                    CH2OH
          |                        |
      H—C—OH                   H—C—OH
          |                        |
      H—C—OH                   H—C—OH
          |                        |
     HO—C—H                   HO—C—H
          |                        |
      H—C—OH                      CO
          |                        |
        CHO                      CH2OH
     d-glucose                 d-fructose
```
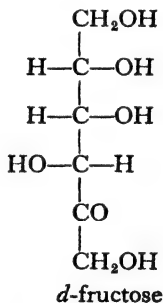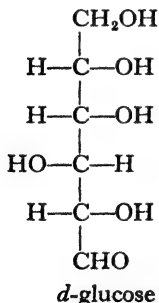
These formulæ must, however, be again modified in accordance with the known reactions of these sugars. It has been shown (p. 354) that glucose is capable of forming an additive compound with methyl or other alcohol, followed by the elimination of a molecule of water to form a closed-chain anhydride called a glucoside. By analogy glucose should be capable of forming an additive compound with water to form a hypothetical aldehydrol, followed by the elimination of the elements of water

from other groups to form a closed-chain anhydride isomeric with the original glucose:

| Hypothetical aldehydrol (4 asymmetric carbon atoms) | α-glucose | β-glucose |

Aldehydic formula for glucose (5 asymmetric carbon atoms)
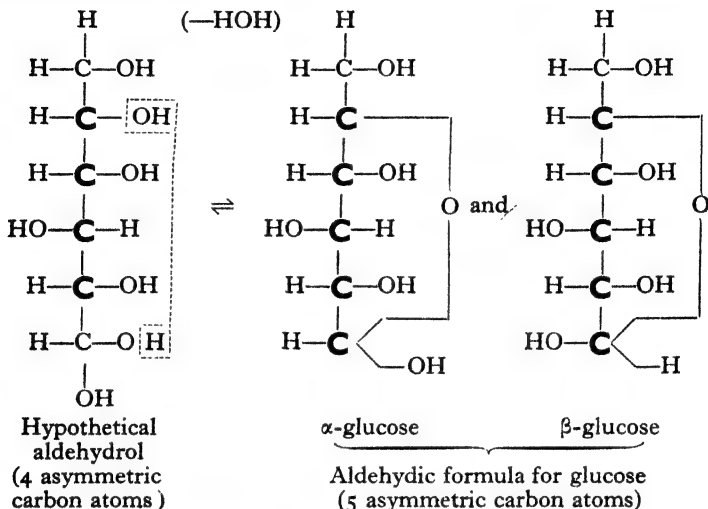
This anhydride may be regarded as a glucoside of water, and should be capable of existing in two isomeric forms, the α-form and the β-form. Now when glucose is dissolved in water it is found that the optical activity diminishes by half when the solution is allowed to stand for some time, indicating that aldehydic glucose has been partially converted into the α- and β-anhydrides. Such an optical change is known as *Muta-rotation.* When equilibrium is reached there exist in the solution three tautomeric forms of glucose, namely, aldehydic glucose, α-glucose, and β-glucose.

The internal cyclic structure of glucose is very unstable and this muta-rotation explains the reactions of glucose with prussic acid, hydroxylamine, and phenylhydrazone. These compounds react with the aldehydic glucose and so disturb the " tautomeric " equilibrium of the solution until all the glucose has been converted to the aldehydic (open-chain) form. In all probability the cyclic structure of glucose comprises a six-atom ring, while fructose, which should also form three tautomeric

substances, contains a five-atom ring or cyclic structure. These two sugars may therefore be represented structurally as follows:

Glucose
(six-atom ring)

Fructose
(five-atom ring)
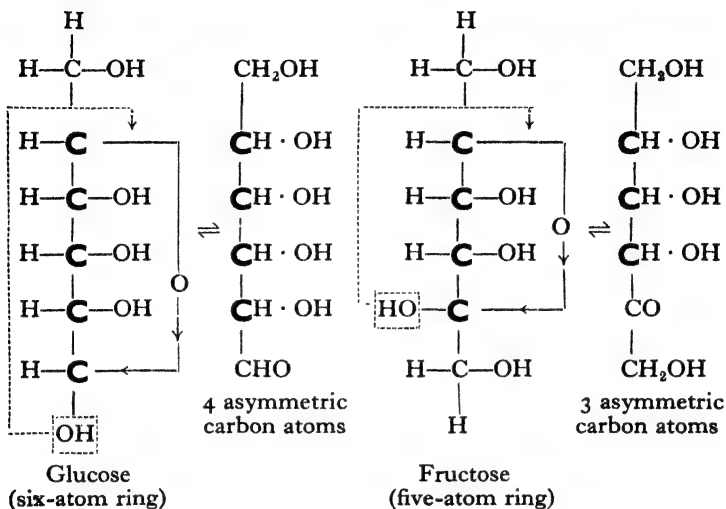
QUESTIONS

1. What evidence as to the constitution of glucose has been furnished by the use of (a) nitric acid, (b) bromine, (c) acetic anhydride, (d) phenylhydrazine?   (*Phar. Chem. Qual.*)

2. Give two examples to illustrate some of the uses to which each of the following reagents is put in organic practice: bromine, hydrogen iodide, phosphorus pentachloride, phenylhydrazine, zinc.

3. What do you understand by (a) a carbohydrate, (b) a sugar, (c) a glucoside? Give examples.

What evidence can you give that glucose (a) is an aldehyde, (b) contains an unbranched chain of six carbon atoms, (c) contains the group —CH_2OH?

4. Briefly summarize the chemistry of dextrose, paying special attention to the reactions which serve to prove the aldose constitution.   (*Chemists and Druggists Qual.*)

5. Give the constitutional formulæ of each of the following: acetone, lactic acid, aceto-acetic acid, glucose.   Describe any distinguishing reactions of these substances.

6. Discuss the composition and properties of liquid glucose showing clearly how it differs from dextrose and from barley sugar.   Give a short account of the principal reactions which occur in the preparation of alcohol from each of these substances.
                    (*Chemists and Druggists Qual.*)

7. Give the experimental evidence which proves that glucose is (*a*) a pentahydric alcohol, (*b*) an aldehyde.   What is the action on glucose of (*a*) Tollen's reagent, (*b*) phenylhydrazine, (*c*) sodium amalgam, (*d*) prussic acid, (*e*) yeast.

8. Give an outline of the evidence by which the constitutional formula of glucose has been established.   (*II. M.B., London.*)

9. Name the chief sources of grape sugar (glucose), cane sugar and starch.   Describe the experiments you would make to distinguish between these three substances in the laboratory. How may glucose be obtained from starch in the laboratory?
                    (*Civil Service: Navy, Army, and Air Force.*)

10. What do you understand by (*a*) a carbohydrate, (*b*) a sugar, (*c*) hydrolysis, (*d*) invert sugar?   Give examples.

11. What are the properties of (*a*) cane sugar, (*b*) glucose, (*c*) starch, (*d*) cellulose?
Describe the manufacture of one of them.

12. Write a short essay on the chemical structure of either tartaric acid or cellulose.   (*Inst. of Patent Agents.*)

13. Discuss the chemistry of one of the following: dyes, sugar, hydrocarbons, cellulose.   (*Inst. of Patent Agents.*)

14. Give the constitutional formula of *d*-glucose.   State clearly how you could distinguish glucose from (*a*) fructose; (*b*) sucrose; (*c*) lactose.   (*II. M.B., London.*)

CHAPTER XV

Aromatic Hydrocarbons

In addition to the aliphatic hydrocarbons there are other compounds which contain carbon and hydrogen only. They have the general formula

$$C_nH_{2n-6}$$

where n is an integer not less than 6.

These compounds are known as **aromatic hydrocarbons.** (The name aromatic was originally given to a set of compounds which possessed a pleasant aroma and included such substances as oil of cloves, oil of turpentine and other essential oils. The name, however, is a misnomer, as some " aromatic " compounds have a most unpleasant smell.) Owing to their distinctive properties they cannot be classified with any of the aliphatic series.

Distinctive Properties of Aromatic Compounds.

1. They contain a higher percentage of carbon than aliphatic compounds:

Benzene, C_6H_6, contains 92·3 per cent of carbon (aromatic)
Hexane, C_6H_{14}, contains 83·7 per cent of carbon (aliphatic)

2. The more complex aromatic compounds may be broken up by the action of various reagents into simpler substances, such as

Benzene	..	..	..	C_6H_6
Phenol	..	..	..	C_6H_5OH
Picric acid	..	..	..	$C_6H_2(NO_2)_3OH,$

containing six carbon atoms; further action in an endeavour to obtain a compound or compounds with a smaller number of carbon atoms usually results in a complete decomposition of the molecule.

3. They all contain the residual nucleus of six carbon atoms.

4. They contain a **closed chain** or **ring** of carbon atoms. Kekulé was the first to suggest a cyclic formula for benzene. It should be noted, however, that many cyclic or closed-chain compounds which contain less than six carbon atoms exist, but these cannot be classified along with the aromatic compounds.

Constitution of Benzene, C_6H_6.

The simplest representative of the aromatic hydrocarbons is benzene, and as its reactions are typical, its constitution will be discussed as a preliminary. Benzene contains six atoms each of carbon and hydrogen. These may be arranged in a straight chain:

$$—CH—CH—CH—CH—CH—CH—,$$
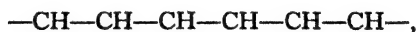
indicating that there are free bonds at the end carbon atoms and at the same time the valencies of the four intermediate carbon atoms are not satisfied. If the above structure is modified by linking the extreme carbon atoms together,

$$\begin{array}{c} CH—CH—CH—CH \\ | \qquad\qquad\quad | \\ CH————————CH, \end{array}$$
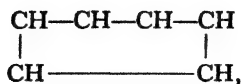
a closed chain or cyclic compound is obtained. A more symmetrical arrangement of the —CH groups leads to a

formula for benzene which can be represented by a regular hexagon:

(a)   (b)   (c)   (d)
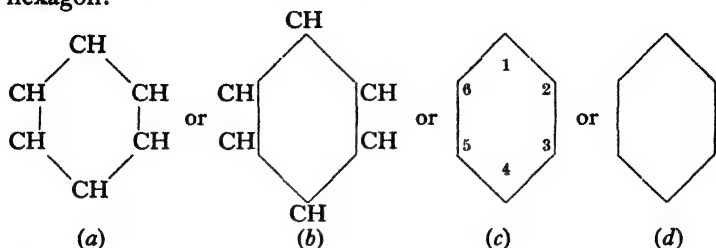
This arrangement is known as Kekulé's hexagon and is based primarily on the phenomena of isomerism. It will be seen that the hydrogen atoms are symmetrically placed and numbered as shown in the regular hexagon (c). In formula (d) the —CH groups are omitted for convenience.*

This formula offers a ready explanation of many of the characteristic properties of benzene. These include its stability towards reagents; the formation of *one* mono-derivative only and of *three* isomeric di-derivatives, such as the dichlorobenzenes $C_6H_4Cl_2$, the dibromobenzenes $C_6H_4Br_2$, the dinitrobenzenes $C_6H_4(NO_2)_2$.

In the three isomeric di-derivatives the substituents occupy positions known as the **ortho-, meta-** and **para-** positions. For example, the dichlorobenzenes have the following formulæ:

Ortho-   Meta-   Para-
dichlorobenzene   dichlorobenzene   dichlorobenzene
Positions   Positions   Positions
1 : 2 and 1 : 6   1 : 3 and 1 : 5   1 : 4, 2 : 5, and 3 : 6
similar   similar   similar
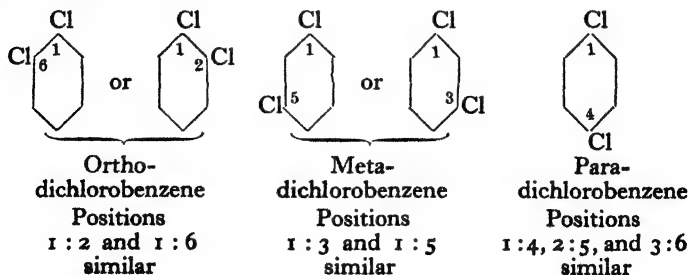
* In order to save space, the hexagon is normally printed in an elongated form.

In the above formula for benzene only three bonds of each carbon atom are utilized; the fourth carbon bond is linked to another carbon atom, thus giving three double bonds:

Kekulé's Formula (1865)
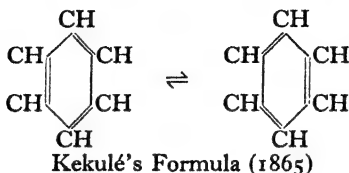
The alternate single and double bonds were inserted by Kekulé, who supposed that these bonds were not fixed but mobile.

This formula represents an unsaturated hydrocarbon of the olefine series and is in perfect harmony with the formation of (*a*) benzene from acetylene, and of (*b*) trimethyl benzene from acetone.

(*a*) Benzene from acetylene:

Acetylene   Benzene

(*b*) Trimethyl benzene from acetone:

$+ \; 3H_2O$
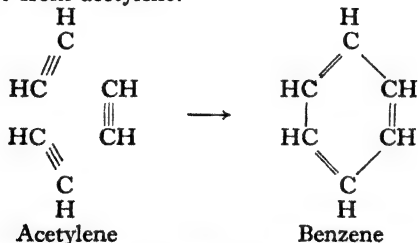
Acetone   Trimethyl benzene
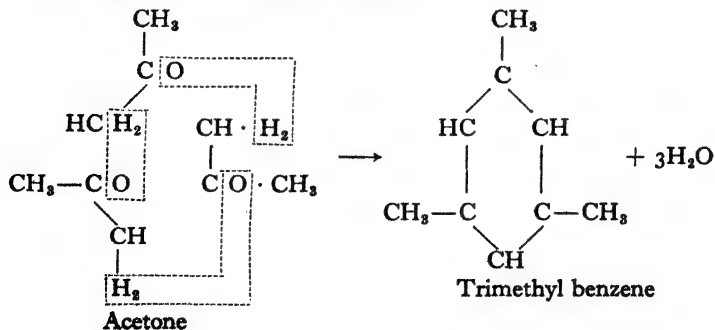
Benzene, in fact, has the properties of an olefine, as it forms additive compounds with hydrogen, chlorine, bromine, hypochlorous acid, &c.:

C_6H_{12} .. .. .. Hexahydrobenzene
$C_6H_6Br_6$ .. .. .. Benzene hexabromide
$C_6H_6Cl_6$ .. .. .. Benzene hexachloride
$C_6H_6(HClO)_3$ .. .. Benzene trichlorhydrin

Since the hydrocarbon C_6H_{12} is still two hydrogen atoms short of complete saturation and yet contains no unsatisfied valencies or bonds, its formula must be written:

Hexahydrobenzene   Hexabromobenzene

, and, similarly,
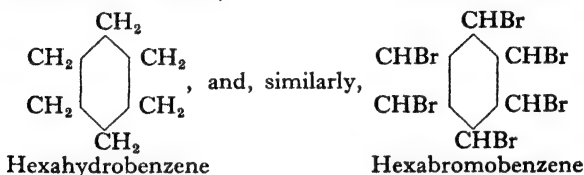
Compounds of this type are known as ring or cyclic hydrocarbons; hexahydrobenzene is also called *cyclo-hexane* or *hexamethylene*.

Arguments against Kekulé's Formula.

1. Two ortho-disubstituted derivatives should be possible; but Kekulé suggested that the single and double bonds may be continually changing.

2. The stability of benzene towards oxidizing agents.

Other Formulæ.—Armstrong and Baeyer suggested that the fourth carbon bond is centric and has a centric, potential, or residual valency.

Benzene   Dihydrobenzene

or
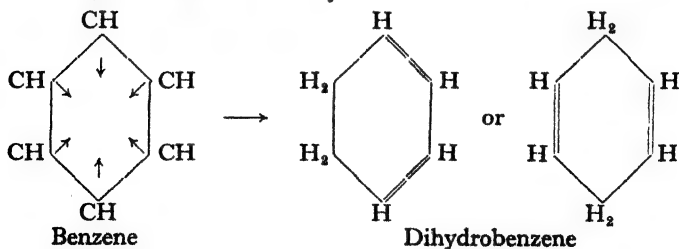
When benzene is reduced to dihydrobenzene four of the six centric bonds form double bonds. This readily accounts for the great difference between the chemical properties of benzene and those of its reduction products.
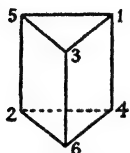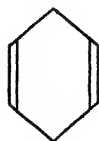
Ladenburg's   Claus's   Dewar's
prism formula   diagonal formula   formula

The three-dimensional formulæ, such as Ladenburg's triangular prism and the regular octahedron, assigned to benzene must be discarded because some of the tri-substituted derivatives would be asymmetric and therefore capable of existing in optically active forms. As a matter of fact, no naturally occurring benzene derivative is optically active and all attempts to resolve benzene derivatives have hitherto been unsuccessful. In consequence, the two-dimensional flat hexagon has now been accepted as the formula for benzene, and this formula has been verified by X-ray crystal analysis, especially that of the compound hexamethyl benzene $C_6(CH_3)_6$, which contains twelve carbon atoms in one plane. According to the flat hexagon formula for benzene, three isomeric di- and tri-derivatives of benzene should exist, and these are all obtained.

Körner's Absolute Method of Orientation (i.e. distinguishing between ortho-, meta-, and para-derivatives).

Körner (1875) utilized the relationship between the isomeric di- and tri-derivatives of benzene in order to identify the ortho-, meta- and para-derivatives of benzene. The hydroxy-derivatives of benzene will serve to illustrate

this method of identification. It must be noted, however, that the hydroxyl group can be displaced by other mono-valent elements or groups, which must be of the same kind.

OH   yields   OH (positions 1, 2, 6) OH   OH (positions 1, 5, 3) OH   OH (positions 1, 4) OH

Hydroxy-benzene or phenol   Ortho-dihydroxy-benzene (catechol)   Meta-dihydroxy-benzene (resorcinol)   Para-dihydroxy-benzene (quinol)

I   **(Para)**

OH (position 1) OH (position 4)

1 : 4 dihydroxy-benzene (quinol)

yields
one   ⟶
tri-derivative

OH (positions 1, 4, 3) OH OH
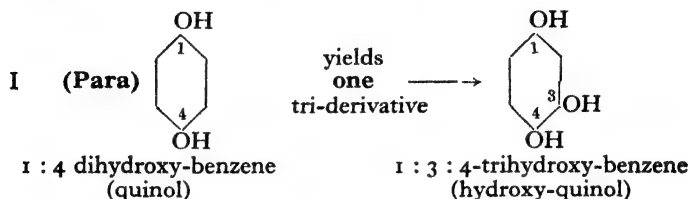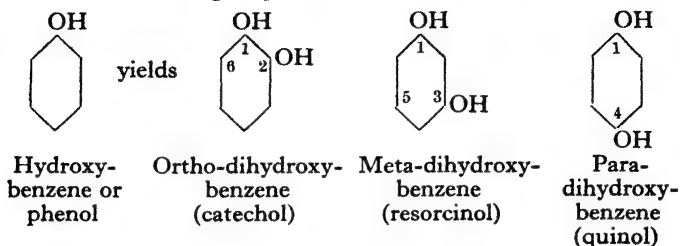
1 : 3 : 4-trihydroxy-benzene (hydroxy-quinol)
The positions
1 : 2 : 4;   1 : 4 : 5; and
1 : 4 : 6 are similar

II **(Ortho)**   OH (positions 1, 6, 2) OH

1 : 2 or 1 : 6
dihydroxy-benzene
(catechol)

yields
two
tri-derivatives

OH (positions 1, 2, 3) OH OH

1 : 2 : 3 trihydroxy-benzene (pyrogallol)

OH (positions 1, 2, 4) OH OH

1 : 2 : 4 trihydroxy-benzene (hydroxy-quinol)

(The position
1 : 2 : 5 is similar)

OH
1 2 OH
3 OH

1 : 2 : 3 trihydroxy-benzene
known as the
Vicinal form (pyrogallol)

OH
1
5 3 OH

III (Meta)
1 : 3 or 1 : 5
dihydroxy-benzene
(resorcinol)

yields
three
tri-derivatives

OH
1
3 OH
4
OH

1 : 3 : 4 trihydroxy-benzene
known as the
Asymmetric form
(hydroxy-quinol)
The position 1 : 3 : 6 is
similar

OH
1
OH 5 3 OH

1 : 3 : 5 trihydroxy-benzene,
known as the
Symmetric form
(phloroglucinol)

These three examples illustrate the following rules, which should be memorized:

I. **Para**- di-derivatives form **one** tri-derivative only, and are known as 1 : 4 compounds.

II. **Ortho**- di-derivatives form **two** tri-derivatives, and are known as 1 : 2 or 1 : 6 compounds.

III. **Meta**- di-derivatives form **three** tri-derivatives, and are known as 1 : 3 or 1 : 5 compounds.

Thiele's Theory of Partial Valencies.

Thiele employed a knowledge of the characteristic properties of unsaturated compounds to account for the stability of the benzene ring.

In the system

$$-CH{=}CH-CH{=}CH-$$

or in its extension

$$-CH{=}CH-CH{=}CH-CH{=}CH-, \&c.,$$

the double bonds were named " Conjugated Double Bonds " by Thiele. He assumed that the single valency bond in such a system can be subdivided, and that in an unsaturated compound like ethylene $CH_2{=}CH_2$ the two bonds are not entirely employed to bind the two carbon atoms together, but a small portion of each is free to combine with other partial bonds, and it is these free valencies which give to the compound its great reactivity. This residual affinity of the carbon atoms is called a " Partial Valency " and may be represented by dotted lines:

(*a*) $CH_2{=}CH_2$ in ethylene, $CH_2{=}CH_2$

(*b*) $-CH{=}CH-CH{=}CH-$ in isoprene,

   $CH_2{=}C(CH_3)-CH{=}CH_2$ or $H-CH{=}C-CH{=}CH-H$
                                                    $\overset{|}{C}H_3$
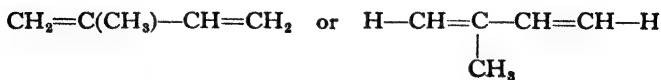
Further, Thiele assumed that the central partial valencies neutralize one another, so that in a " conjugated double

bond " system only the end carbon atoms exhibit chemical activity:

$$—CH{=}CH—CH{=}CH—CH{=}CH—$$
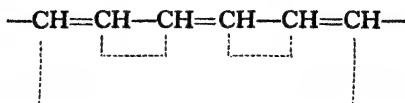
Hence additive products are formed at the end carbon atoms, where there are unsatisfied partial valencies.

In Kekulé's hexagonal formula for benzene there are three conjugated bonds, and according to Thiele's theory each carbon atom has a partial valency; owing to the cyclic structure of benzene these partial valencies neutralize each other entirely, so that three potential valencies are formed and no residual valencies are available. This is in accordance with the stability shown by benzene towards reagents which react with unsaturated compounds. At the same time the potential valencies are available for forming additive products, thus explaining the difference between benzene and a true saturated compound.

Thiele's formula for benzene may be represented as follows:

| Benzene ring, showing conjugated double bonds and partial valencies | Benzene ring, showing partial valencies neutralized to form potential valencies | Benzene ring, showing potential valencies as part of the benzene nucleus |
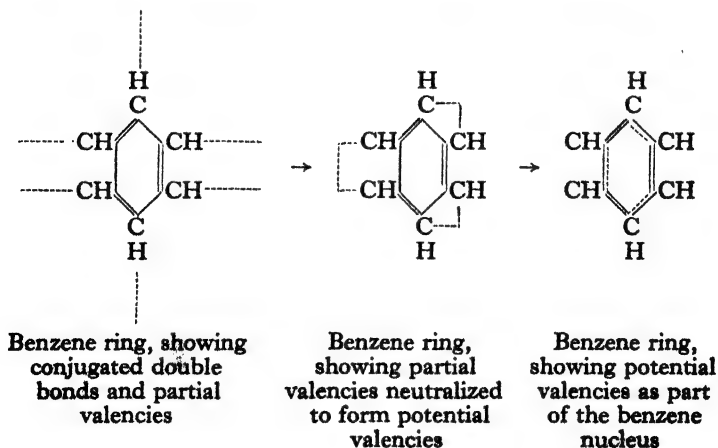
A conjugated compound may be defined as one which contains a series of alternate single and double bonds.

Examples include:

> Acrolein, $CH_2=CH—CH=O$,
> Acrylic acid, $CH_2=CH—C(OH)=O$,
> Isoprene, $CH_2=C(CH_3)—CH=CH_2$,
> Butadiene, $CH_2=CH—CH=CH_2$.

It will be observed that conjugated compounds include certain hydrocarbons and also compounds containing oxygen, &c.

Benzene, C_6H_6.

Benzene was discovered by Faraday in 1825 and detected in coal tar by Hofmann in 1845. (Coal tar, now so valuable as a source of basic materials for chemical industry, was once regarded as a troublesome waste product in gas manufacture).

Formation.

1. *Commercial Method.*

From coal tar distillation. Each ton of coal yields from 10 to 20 gall. of coal tar. Coal tar has the following approximate percentage composition:

Benzene and homologues	2–8
Carbolic oil	8–10
Carbolic acid	0·15–0·25
Creosote oil	8–10
Anthracene oil	14–20
Heavy oil	5–10
Pitch	45–55
Water	12–15

On distillation from a wrought iron still the following fractions are obtained:

COAL TAR PRODUCTS

Distillate	Specific Gravity	Temperature	Constituents
1. Light oil or crude naphtha	0·9–0·95	To 170° C.	Benzene, toluene, xylene.
2. Carbolic oil or middle oil	1·01	170°–240°	Phenol and naphthalene.
3. Creosote oil or first heavy oil	1·04	240°–270°	Various, not usually separated.
4. Anthracene oil or green oil	1·10	270°–350°	Anthracene and carbazole.
5. Second heavy oil	1·15 +	350°–450°	Various, not usually separated.
6. Pitch	1·5 +	(Residue)	Various.

The benzene of commerce, known as " benzol ", is a mixture of the hydrocarbons comprising the first distillate and also thiophene, C_4H_4S. Pure benzene is obtained by fractionating " benzol " and collecting the fraction which boils at 80°–85° C. This fraction is cooled; benzene separates in the form of crystals and is removed. The thiophene, which is also deposited, is separated from the benzene by the prolonged action of concentrated sulphuric acid.

2. *Laboratory Method.*—By distilling a mixture of calcium benzoate or phthalic acid with twice its weight of soda-lime:

$$\begin{array}{c} C_6H_5COO \\ C_6H_5COO \end{array}\!\!\Big\rangle Ca + Ca\!\Big\langle\begin{array}{c} OH \\ OH \end{array} = 2C_6H_6 + 2CaCO_3$$

Calcium benzoate

$$C_6H_4\!\Big\langle\begin{array}{c} COOH \\ COOH \end{array} + 2Ca\!\Big\langle\begin{array}{c} OH \\ OH \end{array} = C_6H_6 + 2CaCO_3 + 2H_2O$$

Phthalic acid
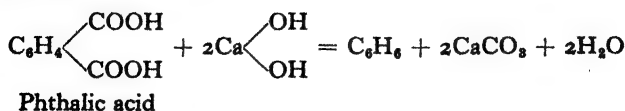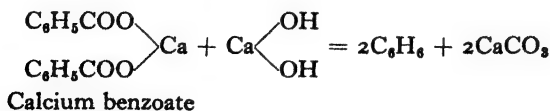
The distillate obtained contains water and impure benzene. These liquids can be separated in a separating funnel, and the brownish-coloured benzene is dried over solid calcium chloride and redistilled.

3. *Synthetic Method.*—By heating acetylene in a closed vessel at a moderately low temperature:

$$6C + 3H_2 = 3C_2H_2 = C_6H_6$$
$$\qquad\qquad\text{Acetylene}\quad\text{Benzene}$$

4. By boiling a diazonium salt (p. 401) with absolute alcohol:

$$C_6H_5N : N—Cl + CH_3CH_2OH = C_6H_6 + CH_3CHO + HCl + N_2$$
Phenyl diazonium   Ethyl   Acetaldehyde
      chloride   alcohol
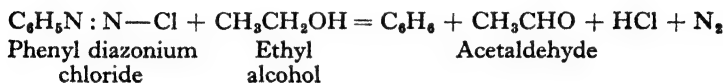
5. By Grignard's method (p. 478).

Properties.—Colourless mobile liquid, b. pt. 80·5° C., m. pt. 5·4° C., sp. gr. 0·874. It freezes to white crystals at 0° C. It has a characteristic smell, and burns with a luminous smoky flame. It is insoluble in water and, being specifically lighter, floats on its surface. It is a good solvent for fats, resins, iodine, phosphorus, sulphur, &c. It is added to motor spirit as an " anti-knock " constituent. It is not acted on by ordinary reducing and oxidizing agents.

Reactions.— 1. It is decomposed into diphenyl and hydrogen when passed through a hot tube:

$$2C_6H_6 = C_6H_5 \cdot C_6H_5 + H_2$$
$$\qquad\qquad\text{Diphenyl}$$
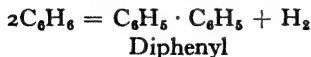
2. On reduction it is converted into a hexahydride (cyclohexane, hexamethylene):

$$C_6H_6 + 3H_2 = C_6H_{12}$$
$$\qquad\qquad\text{Cyclo-}$$
$$\qquad\qquad\text{hexane}$$
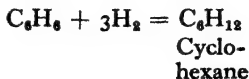
The reduction is brought about by passing a mixture of

benzene vapour and hydrogen over finely divided nickel at 160° C. This reaction indicates that benzene is unsaturated, since it can form additive compounds.

3. It forms additive compounds with chlorine and bromine in the presence of sunlight. These compounds exhibit stereo-isomerism, e.g. the benzene hexachlorides $C_6H_6Cl_6$ have melting-points of 157° and 310° C. respectively; the benzene hexabromides $C_6H_6Br_6$ have melting-points of 212° and 253° C. respectively. These compounds form asymmetric trichlorobenzene and tribromobenzene respectively when heated alone or with alcoholic potash or potassium cyanide:

$$C_6H_6Cl_6 + 3KOH = C_6H_3Cl_3 + 3KCl + 3H_2O$$
<div align="center">Trichloro-
benzene</div>
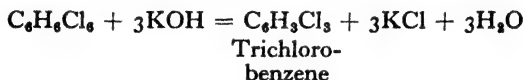
4. It also forms an additive compound with ozone, *triozonide*, $C_6H_6O_9$. This compound on hydrolysis is converted into glyoxal and hydrogen peroxide:

$$C_6H_6O_9 + 3HOH = 3 \begin{vmatrix} CHO \\ CHO \end{vmatrix} + 3H_2O_2$$
<div align="center">Triozonide   Glyoxal</div>
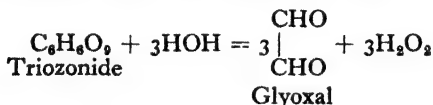
5. It forms substituted products with chlorine and bromine in the presence of a " halogen carrier ", such as iron or iodine. The substitution is progressive until the six hydrogen atoms in the benzene ring are entirely displaced. Iodine alone does not react with benzene (see p. 471):

$$C_6H_6 + Cl_2 = C_6H_5Cl + HCl$$
<div align="center">Mono-
chlorobenzene</div>

$$C_6H_5Cl + Cl_2 = C_6H_4Cl_2 + HCl,$$
<div align="center">Dichloro-
benzene</div>
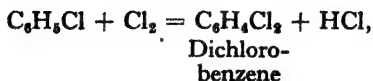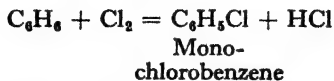
and so on. These aromatic halogen derivatives are more

stable than the corresponding aliphatic compounds; they are not usually attacked by alkalis or ammonia.

For practical details, see p. 585.

6. It forms substituted products with nitric and sulphuric acids. The reaction with concentrated nitric acid is known as **nitration.** The substitution is progressive until trinitrobenzene is obtained.

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$$
Nitrobenzene
(a liquid, b. pt. 210° C.)

$$C_6H_5NO_2 + HNO_3 = C_6H_4(NO_2)_2 + H_2O$$
m-dinitrobenzene
(a colourless solid, m. pt. 90° C.)

$$C_6H_4(NO_2)_2 + HNO_3 = C_6H_3(NO_2)_3 + H_2O$$
s-trinitrobenzene
(colourless solid, m. pt. 122° C.)
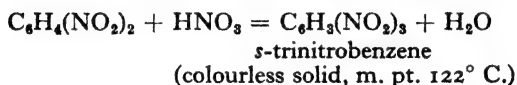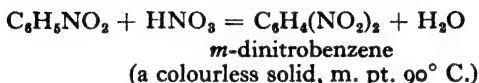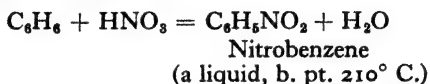
Nitration is usually brought about by a mixture of nitric acid and concentrated sulphuric acid; the latter absorbs the water formed in the reaction.

The reaction with concentrated sulphuric acid is known as **sulphonation.** In this case only a mono-substituted product is formed even after boiling for several hours. Further sulphonation may be brought about by means of fuming sulphuric acid:

$$C_6H_5SO_2OH + H_2SO_4 = C_6H_4(SO_2OH)_2 + H_2O$$
Benzene
di-sulphonic
acid
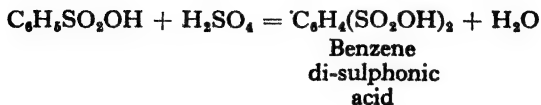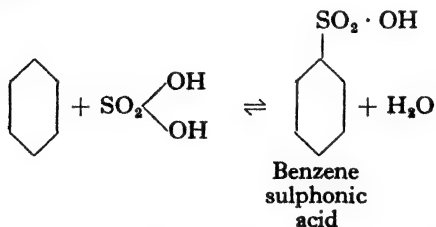
Notes.—(*a*) In these reactions the nitrogen or sulphur is attached to the benzene ring directly, and not by means of an oxygen atom.

(*b*) These reactions are characteristic of aromatic hydrocarbons and other aromatic compounds and serve to differentiate aromatic hydrocarbons from aliphatic.

Nitrobenzene, $C_6H_5NO_2$. Pale yellowish oil, m. pt. 5·7° C., b. pt. 210° C., sp. gr. 1·20. It has an odour of oil of bitter almonds and is poisonous. It burns in air and can be nitrated and sulphonated in the meta-position. On reduction it is converted into

(*a*) Aniline, $C_6H_5NH_2$, in acid solution.

(*b*) β-phenylhydroxylamine, $C_6H_5 \cdot NH \cdot OH$, by neutral reducing agents such as aluminium amalgam.

(*c*) Hydrazobenzene, $C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$, by alkaline reducing agents. At the same time other intermediate products containing two benzene rings are obtained:

$$C_6H_5NO_2 \longrightarrow C_6H_5-\overset{\overset{\textstyle O}{\|}}{N}=NC_6H_5$$

Nitrobenzene   Azoxybenzene

$$\longrightarrow C_6H_5-N=N \cdot C_6H_5 \longrightarrow C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$$

Azobenzene   Diphenylhydrazine or
                        Hydrazobenzene
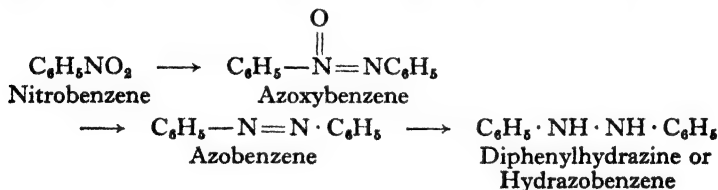
Nitrobenzene is used in the manufacture of aniline and as a cheap scent in soap manufacture.

Benzene Sulphonic Acid, $C_6H_5 \cdot SO_2OH$, is usually obtained in the form of an acid syrup, although it may be prepared in a crystalline form. It is very stable towards alkalis and acids but can form neutral crystalline salts with alkalis under certain conditions. These salts are known as **sulphonates.**

$$C_6H_5SO_2OH + NaOH = C_6H_5SO_2ONa + HOH$$

Sodium benzene
sulphonate
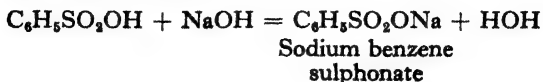
Sulphonates are important because they can be converted into:

A. **Phenols** by fusion with caustic alkalis:

$$C_6H_5 \cdot SO_2 \cdot ONa + NaOH = C_6H_5OH + Na_2SO_3$$
<div align="center">Phenol</div>
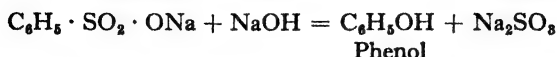
This reaction illustrates the substitution of an $-SO_3H$ group by a hydroxyl $-OH$ group.

B. **Cyanides** by fusion with alkali cyanides:

$$C_6H_5 \cdot SO_2 \cdot ONa + NaCN = C_6H_5CN + Na_2SO_3$$
<div align="center">Phenyl
cyanide</div>
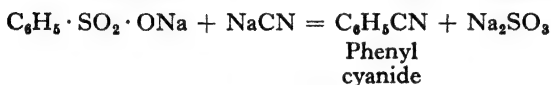
C. **Sulphonic Chlorides** by the action of phosphorus pentachloride:

$$C_6H_5 \cdot SO_2 \cdot ONa + PCl_5 = C_6H_5 \cdot SO_2 \cdot Cl + POCl_3 + NaCl$$
<div align="center">Benzene
sulphonic chloride</div>
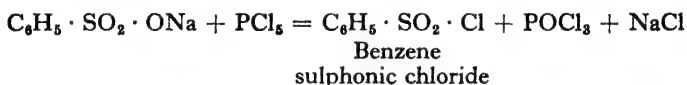
D. **Sulphonamides** by treating sulphonic chlorides with ammonia:

$$C_6H_5 \cdot SO_2 \cdot Cl + NH_3 = C_6H_5 \cdot SO_2 \cdot NH_2 + HCl$$
<div align="center">Benzene
sulphonamide</div>
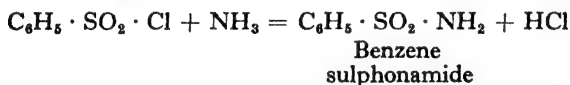
Sulphonic chlorides are employed in organic analysis to identify:

(*a*) Amines.

They react with (1) primary amines to form compounds, e.g. $C_6H_5 \cdot SO_2 \cdot NH \cdot CH_3$, benzene methyl sulphonamide, which are soluble in alkalis; (2) secondary amines to form compounds, e.g. $C_6H_5 \cdot SO_2 \cdot N(CH_3)_2$, benzene dimethyl sulphonamide, which are insoluble in alkalis; while (3) tertiary amines do not form sulphonamides.

(*b*) Alcohols.

(*c*) Hydrocarbons and sulphonates, from which they are formed.

The preparations of (1) bromobenzene, (2) chlorobenzene, (3) nitrobenzene, (4) *m*-dinitrobenzene, (5) benzene sulphonic acid are described in Chap. XXVI (p. 585 *et seq.*)

Toluene, Methyl Benzene, Phenyl Methane, $C_6H_5 \cdot CH_3$.

Occurrence.—Toluene is found in the resin known as Tolu balsam, from which it received its name. It is also found in coal tar.

Formation.

1. By the distillation of Tolu balsam and other resins.

2. By the distillation of coal tar naphtha and of certain petroleums.

3. *Fittig's Method.*—By the action of sodium on a mixture of bromobenzene and methyl iodide in dry ether:

$$C_6H_5 \overline{|Br + Na|} + \overline{|Na + I|} \cdot CH_3 = C_6H_5 \cdot CH_3 + NaBr + NaI$$

The sodium salts formed in this reaction are precipitated and the toluene is decanted off and subjected to fractional distillation. This method is important in organic synthesis; it serves to illustrate the constitution of toluene and to form other aromatic hydrocarbons. For example:

$$C_6H_4 \underset{\overline{|Br + Na|}}{\overset{CH_3}{<}} + \overline{|Na + I|} \cdot CH_3 = C_6H_4 \underset{CH_3}{\overset{CH_3}{<}} + NaBr + NaI$$
<center>Xylene</center>
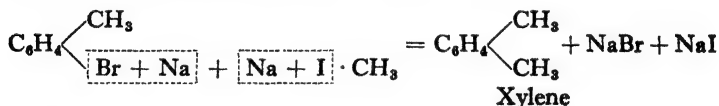
The methyl groups can be replaced by other alkyl groups, yielding simple or mixed homologues of benzene.

4. *Friedel and Crafts' Method.*—By the action of benzene on methyl chloride or bromide in the presence of anhydrous aluminium chloride:

$$C_6H_6 + CH_3Cl \underset{(AlCl_3)}{=} C_6H_5 \cdot CH_3 + HCl$$
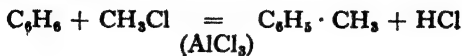
The anhydrous aluminium chloride is first added to the benzene and the methyl chloride or bromide is then passed into the mixture. The aluminium chloride probably acts as a catalyst, although it is possible that it forms an intermediate compound with benzene, which is then decomposed by the methyl chloride. Further action leads to the introduction of additional methyl groups into the benzene nucleus. Various aromatic hydrocarbons can be obtained by substituting other alkyl halides for methyl chloride. For example:

$$C_6H_6 + C_2H_5Br = C_6H_5 \cdot C_2H_5 + HBr$$
$$\text{Ethyl benzene}$$
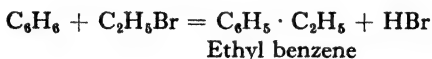
This method is also of considerable importance in organic synthesis, and serves to determine the structure of toluene, and to differentiate the aromatic hydrocarbons from the aliphatic hydrocarbons, which do not react in this way.

Note.—Other examples of Friedel and Crafts' reaction are as follows:

(a) **Acetophenone** (p. 439) is formed from acid chlorides and benzene:

$$C_6H_6 + CH_3COCl = C_6H_5 \cdot CO \cdot CH_3 + HCl$$
$$\text{Acetophenone or}$$
$$\text{Phenyl methyl}$$
$$\text{ketone}$$
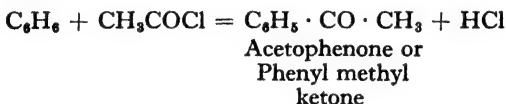
(b) **Triphenylmethane** from chloroform and benzene:

$$3C_6H_6 + CHCl_3 = CH(C_6H_5)_3 + 3HCl$$
$$\text{Triphenyl-}$$
$$\text{methane}$$
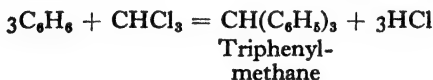
(c) **Triphenyl methyl chloride** from carbon tetrachloride and benzene:

$$3C_6H_6 + CCl_4 = (C_6H_5)_3 \cdot CCl + 3HCl$$
$$\text{Triphenyl}$$
$$\text{methyl}$$
$$\text{chloride}$$
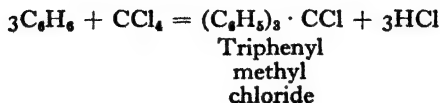
(*d*) **Diphenylmethane** is formed from benzal chloride and benzene, using aluminium amalgam as the catalyst:

$$C_6H_6 + C_6H_5CH_2Cl = C_6H_5 \cdot CH_2 \cdot C_6H_5 + HCl$$

<div align="center">
Benzal   Diphenylmethane
chloride
</div>
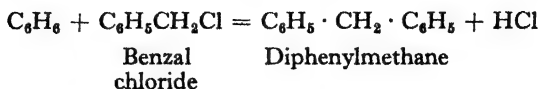
5. By distilling pure toluic acid or calcium toluate with soda lime. Pure toluene is obtained by this method:

$$C_6H_4(CH_3)COOH = C_6H_5CH_3 + CO_2$$

<div align="center">
Toluic acid   Toluene
</div>
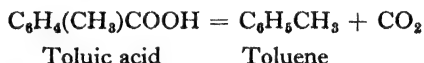
6. By Grignard's method (see p. 479).

Properties.—A colourless mobile liquid, sp. gr. 0·882 at 0° C., b. pt. 110° C. It does not solidify even at −28° C., and cannot, therefore, be purified by crystallization.

It resembles benzene very closely in most respects, differing from it principally in those properties which are due to the presence of the methyl group.

Reactions.—1. With nitric acid and with sulphuric acid its behaviour is similar to that of benzene, i.e. it yields nitro derivatives and sulphonic acids; these compounds exist in three isomeric forms:
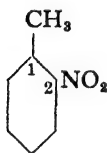
<div align="center">
Ortho-nitrotoluene   Meta-nitrotoluene   Para-nitrotoluene
(1 : 2)   (1 : 3)   (1 : 4)
</div>
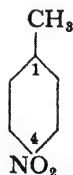
2. The presence of the methyl group, however, causes toluene to exhibit some of the properties of a paraffin. The hydrogen of this group may be displaced by chlorine

(see 5, below), which in turn can be displaced by an —OH or —NH$_2$ group, e.g.

$C_6H_5CH_3 \rightarrow C_6H_5 \cdot CH_2Cl \rightarrow C_6H_5 \cdot CH_2OH \rightarrow C_6H_5 \cdot CH_2 \cdot NH_2$,
Toluene   Benzyl chloride   Benzyl alcohol   Benzylamine
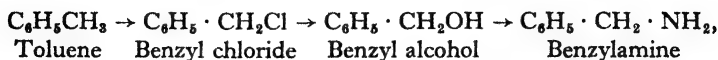
by methods exactly similar to those employed in bringing about these changes in aliphatic compounds.

3. Oxidizing agents, e.g. nitric acid and chromic anhydride, convert the side chain (p. 403) into a carboxyl group,

CH$_3$ (HNO$_3$)   COOH

$+ 3O = \quad + H_2O$

Toluene   Benzoic acid
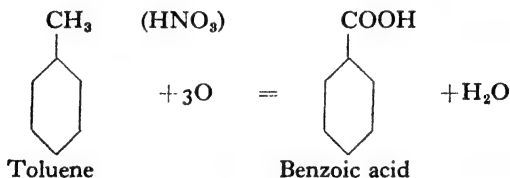
4. Chromyl chloride converts toluene into benzaldehyde, $C_6H_5 \cdot CHO$. The same result is produced if the side chain is an ethyl, propyl, or other alkyl group containing several carbon atoms; the benzene nucleus (p. 403) remains intact.

CH$_3$ (CrO$_2$Cl$_2$)   CHO

$+ 2O = \quad + H_2O$

Toluene   Benzaldehyde
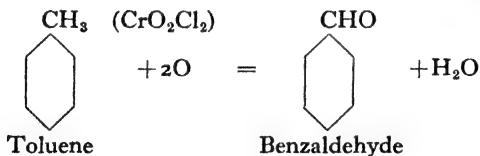
5. Chlorine and bromine can replace hydrogen both in the side chain and in the nucleus.

A. Chlorine passed into *boiling toluene* replaces the hydrogen atoms in the side chain as follows:

$C_6H_5 \cdot CH_2Cl$	$C_6H_5 \cdot CHCl_2$	$C_6H_5 \cdot CCl_3$
Benzyl chloride	Benzal or Benzylidene chloride	Benzotrichloride or Benzenyl chloride
Radicle	Radicle	Radicle
Benzyl	**Benzylidene**	**Benzenyl**
$C_6H_5 \cdot CH_2—$	$C_6H_5 \cdot CH=$	$C_6H_5 \cdot C\equiv$
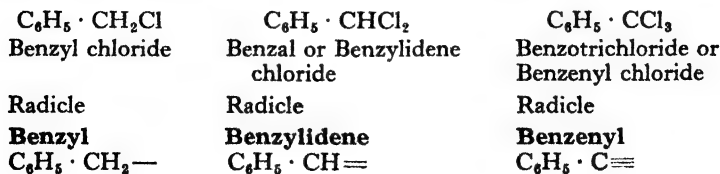
Experiment.—To prepare Benzyl Chloride, $C_6H_5CH_2Cl$, *from Toluene*. A retort of capacity about 250 c.c. is weighed. 50 gm. of toluene are introduced into the retort, which is placed on a sand bath in such a position that the neck of the retort is tilted upwards at an angle of about 45°. This neck is connected to an inclined reflux condenser. Fitted to the tubulus of the retort is an inlet tube as shown in fig. 39. The retort is heated gently until the toluene begins to boil; at this stage dry chlorine is bubbled slowly through the boiling toluene. The chlorine is absorbed; this is indicated by the liquid turning yellow. Volumes of hydrogen chloride are evolved at the same time. The chlorine is allowed to pass until the contents of the retort have gained 18 to 19 gm. in weight, i.e. the theoretical amount calculated from the following equation:

$C_6H_5 \cdot CH_3 + Cl_2 = C_6H_5 \cdot CH_2Cl + HCl$

   92 gm. toluene $\equiv$ 126·5 gm. benzyl chloride (34·5 gm. increase)
$\therefore$ 50 gm. toluene $\equiv$ 18·75 gm. increase in weight

The retort is removed periodically in order to ascertain the increase in weight. When the reaction is complete the contents are removed to a distilling flask and distilled. The first portion which distils over consists of unchanged toluene and is rejected. The fraction boiling between 165° C. and 185° C. is collected and redistilled, and the fraction boiling around 176° C. is then collected; it consists of almost pure benzyl chloride. About 40 gm. should be obtained.

Notes.—1. The chlorine is prepared by the action of strong hydrochloric acid on granulated manganese dioxide and dried by passing the gas through a wash-bottle containing concentrated sulphuric acid.

2. A calcium chloride tube is fitted to the upper end of the condenser to absorb moisture and fumes.

3. The experiment should be conducted in a fume cupboard if possible, as the vapour of benzyl chloride affects the membranes of the eyes and nose.

Benzyl chloride is a colourless liquid with an irritating smell, b. pt. 176°, sp. gr. 1·107.
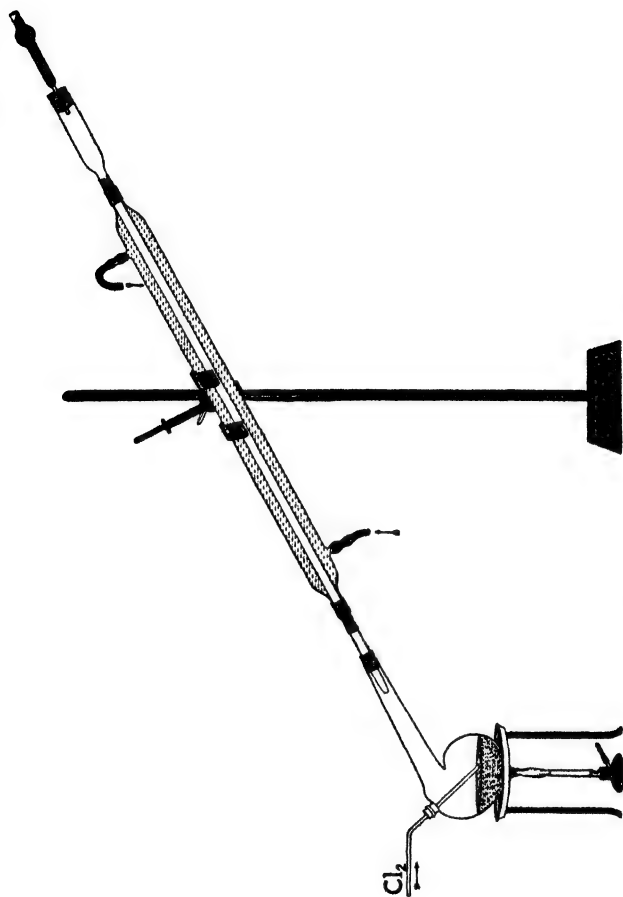
Fig. 39.—Preparation of Benzyl Chloride

B. Chlorine passed into *cold toluene* replaces the hydrogen atoms in the nucleus, provided that a " halogen carrier " such as iodine, phosphorus or iron is present.   Mono-, di-, tri-, &c., chlorotoluenes are formed.   The mono-chlorotoluenes exist in three isomeric forms:
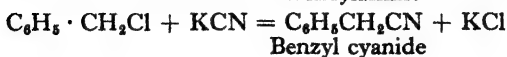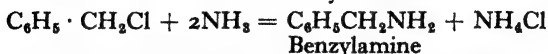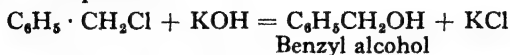
CH$_3$	CH$_3$	CH$_3$	CH$_2$ · Cl.
Ortho-chlorotoluene	Meta-chlorotoluene	Para-chlorotoluene	Benzyl chloride
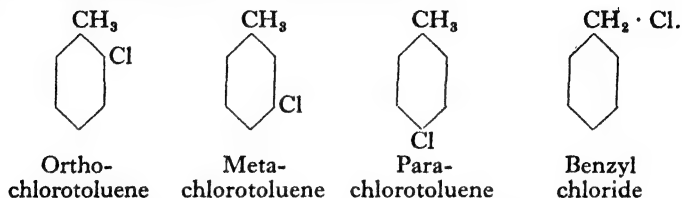
Benzyl chloride is also isomeric with the chlorotoluenes.

On oxidation each of these isomeric compounds is converted into the corresponding chlorobenzoic acid, whilst benzyl chloride is converted into benzoic acid:

COOH	COOH	COOH	COOH
o-chlorobenzoic acid	*m*-chlorobenzoic acid	*p*-chlorobenzoic acid	Benzoic acid
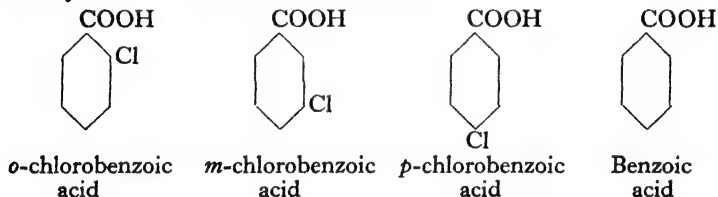
The side chain in each of these compounds is completely oxidized, irrespective of whether the hydrogen atoms in the side chain have been replaced by other radicles or not. (In all aromatic compounds the side chain is easily oxidized without the nucleus being affected.)

The halogen in the nucleus is very difficult to remove, whereas that in the side chain behaves like the halogen in aliphatic compounds:

$$C_6H_5 \cdot CH_2Cl + KOH = C_6H_5CH_2OH + KCl$$
<div align="center">Benzyl alcohol</div>

$$C_6H_5 \cdot CH_2Cl + 2NH_3 = C_6H_5CH_2NH_2 + NH_4Cl$$
<div align="center">Benzylamine</div>

$$C_6H_5 \cdot CH_2Cl + KCN = C_6H_5CH_2CN + KCl$$
<div align="center">Benzyl cyanide</div>

Experiment.—Shake a little bromobenzene, benzyl chloride, and ethyl bromide in separate test tubes with an alcoholic solution of silver nitrate and notice the rate at which the silver halide is formed in each case. What information is deduced from this experiment?

A very important general method for the preparation of aromatic halogen derivatives containing the halogen in the nucleus consists in the decomposition of the *diazonium salts*, e.g.

$$C_6H_6 \rightarrow C_6H_5NO_2 \rightarrow C_6H_5NH_2 \rightarrow C_6H_5N:N \cdot Cl \rightarrow C_6H_5Cl$$

| Benzene | Nitro-benzene | Aniline | Phenyl diazonium chloride | Chloro-benzene |
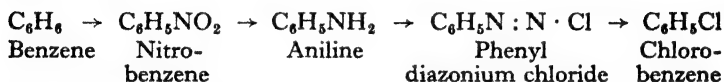
The benzene is first converted into nitrobenzene by a mixture of nitric and sulphuric acids. The nitrobenzene is then reduced to aniline, by nascent hydrogen generated from iron and hydrochloric acid or by tin and hydrochloric acid:

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O$$

Nitrobenzene   Aniline
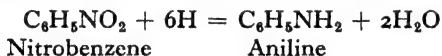
The aniline is converted into aniline hydrochloride by hydrochloric acid, and this compound on treatment with nitrous acid is diazotized, that is, converted into a substituted ammonium salt:

$$C_6H_5 \cdot N \underset{Cl}{\overset{H_3}{<}} + \underset{O}{\overset{HO}{>}} N = C_6H_5 \cdot N \underset{Cl}{\overset{N}{<}} + 2H_2O$$

$$C_6H_5 \cdot NH_2 \cdot HCl + HNO_2 = C_6H_5 \cdot N{=}N \cdot Cl + 2H_2O$$

Phenyl
(or Benzene)
diazonium chloride

(Compare $H \cdot N \underset{Cl}{\overset{H_3}{<}}$, ammonium chloride).
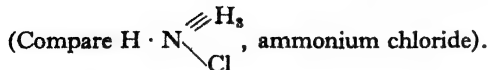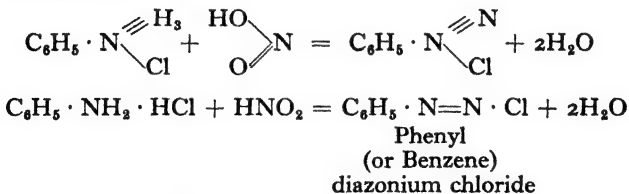
The product is called Phenyl (or Benzene) diazonium chloride (see p. 470; for the alternative formulæ, see p. 473).

The diazonium compound is then converted into chlorobenzene by *Sandmeyer's Reaction*, which consists in warming the diazonium salt with a solution of cuprous chloride in hydrochloric acid. Nitrogen is evolved, and the salt is decomposed:

$$C_6H_5N : N \cdot Cl = C_6H_5Cl + N_2$$
Chloro-
benzene
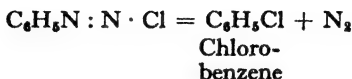
Sandmeyer's reaction may be further extended, for by substituting cuprous bromide, cuprous cyanide, &c., for the chloride and using the appropriate acid, the corresponding bromo-, cyano- and other derivatives of benzene may be obtained:

$$2C_6H_5N : N \cdot Cl + Cu_2Br_2 = 2C_6H_5Br + Cu_2Cl_2 + 2N_2$$
Bromo-
benzene

$$2C_6H_5N : N \cdot Cl + Cu_2(CN)_2 = 2C_6H_5CN + Cu_2Cl_2 + 2N_2$$
Phenyl cyanide
or Cyanobenzene
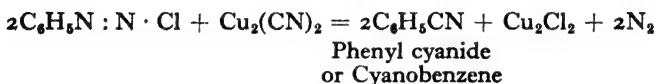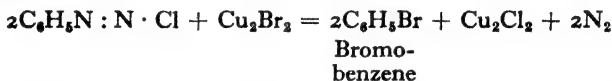
The copper salts employed undoubtedly form additive compounds with the diazo-compound; these immediately decompose to form the benzene derivative.

In the same way monochlorotoluene can be prepared from toluene:

$$C_6H_5CH_3 \longrightarrow C_6H_4\Big\langle{}^{CH_3}_{NO_2} \longrightarrow C_6H_4\Big\langle{}^{CH_3}_{NH_2} \longrightarrow$$
Toluene   Nitrotoluene   Toluidine

$$C_6H_4\Big\langle{}^{CH_3}_{N : N \cdot Cl} \longrightarrow C_6H_4\Big\langle{}^{CH_3}_{Cl}$$
Toluene diazonium   Mono-
chloride   chlorotoluene
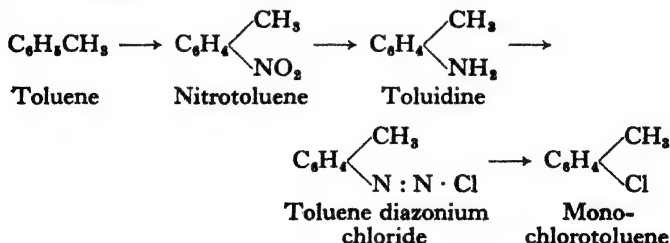
Constitution of Toluene.

The structure of toluene may be represented as follows:

Methyl benzene   or   Phenyl methane
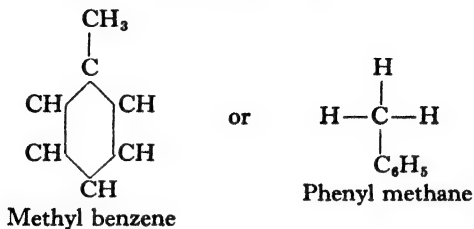
The first formula indicates that the toluene molecule consists of two parts:

1. The **Benzenoid** part or **Nucleus** C_6H_5—

2. The **Aliphatic** part or **Side chain** CH_3—

It is clear that toluene may be regarded as:

(a) A substituted product of benzene, in which one hydrogen atom of the benzene nucleus has been displaced by a monovalent methyl group, hence the name methyl benzene.

(b) A substituted product of methane, in which one hydrogen atom has been displaced by a monovalent phenyl group, hence the name phenyl methane.

The name **phenyl** for the benzene radicle $—C_6H_5$ is derived from the Greek φαίνω (*phaino*), to illuminate, on account of the connexion of benzene with the manufacture of coal gas.

The term was first used by Laurent (1841) in *hydrate de phényle* and *acide phénique*, names for the substance now called phenol.

The preparation of toluene from bromobenzene and methyl iodide shows that toluene is formed by the direct linking of a phenyl group and a methyl group.

Benzal Chloride, Benzylidene Chloride, $C_6H_5CHCl_2$, and Benzotrichloride, Benzenyl Chloride, Phenyl Chloroform, $C_6H_5CCl_3$.

Formation.

1. By chlorination of toluene, precisely as outlined for benzyl chloride (p. 398). With 50 gm. of toluene, benzal chloride and benzotrichloride are formed when the increases in weight are 37·5 gm. and 56·2 gm. respectively:

$$C_6H_5CH_3 + 2Cl_2 = C_6H_5CHCl_2 + 2HCl,$$
$$C_6H_5CH_3 + 3Cl_2 = C_6H_5CCl_3 + 3HCl.$$

2. By the action of phosphorus pentachloride on

(*a*) Benzaldehyde (p. 437) to form benzal chloride:

$$C_6H_5CHO + PCl_5 = C_6H_5CHCl_2 + POCl_3$$
Benzaldehyde
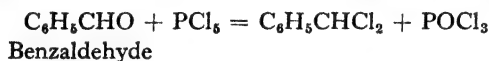
(*b*) Benzoic acid (p. 422) or benzoyl chloride (p. 427) to form benzotrichloride:

$$C_6H_5COOH + 2PCl_5 = C_6H_5CCl_3 + 2POCl_3 + HCl,$$
Benzoic acid

$$C_6H_5COCl + PCl_5 = C_6H_5CCl_3 + POCl_3.$$
Benzoyl chloride
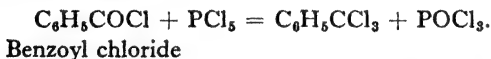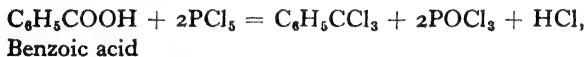
Properties.—Benzal chloride is a colourless liquid, sp. gr. 1·295, b. pt. 206° C. It is used in organic synthesis and in the preparation of benzaldehyde.

Benzotrichloride is a colourless liquid, sp. gr. 1·380, b. pt. 213° C. It is used in the manufacture of benzoic acid.

Reactions.—1. On boiling with sodium carbonate solution they are converted into benzaldehyde and benzoic acid respectively:

$$C_6H_5CHCl_2 + Na_2CO_3 = C_6H_5CHO + 2NaCl + CO_2,$$
$$2C_6H_5CCl_3 + 3Na_2CO_3 + H_2O = 2C_6H_5COOH + 6NaCl + 3CO_2$$
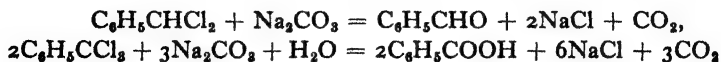
2. On treatment with superheated water benzaldehyde and benzoic acid respectively are formed. This is the commercial method for making benzoic acid. In the case of the trichloride, boiling with lime (p. 423) may be used instead.

$$C_6H_5CHCl_2 + HOH = C_6H_5CHO + 2HCl,$$
$$C_6H_5CCl_3 + 2HOH = C_6H_5COOH + 3HCl.$$
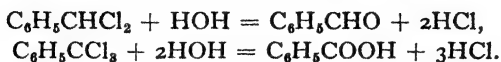
3. On oxidation with nitric acid they are both converted into benzoic acid:

$$C_6H_5CHCl_2 + 2HNO_3 = C_6H_5COOH + 2HCl + 2NO_2,$$
$$C_6H_5CCl_3 + 4HNO_3 = C_6H_5COOH + 3HCl + 4NO_2 + O_2.$$
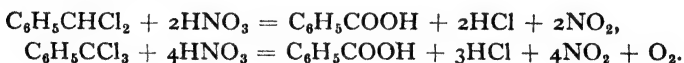
Xylene, Dimethyl Benzene, Methyl Toluene, $C_6H_4(CH_3)_2$.

Occurrence.—In coal tar and petroleum. The distilled product contains three xylenes: 92 per cent meta, 5–8 per cent ortho, 1·5–2 per cent para.

Formation.

1. From coal tar or petroleum.

The three isomers cannot be separated from one another by fractional distillation, as their boiling-points lie too close together: ortho-xylene boils at 142° C., meta-xylene at 138° C., para-xylene at 137° C.

The xylenes obtained from the distillation of coal tar or petroleum are separated by treatment with sulphuric acid; ortho- and meta-xylene dissolve, forming sulphonic acids, but para-xylene does not. The para-xylene is separated by distillation, and the ortho- and meta-sulphonic acids are separated from one another by fractional crystallization of their sodium salts; the sodium salt of *o*-xylene sulphonic acid is less soluble in water than the sodium salt of *m*-xylene sulphonic acid. The respective xylenes are then obtained from the separated sodium salts by treatment with mineral acids; this sets free the corresponding sulphonic

acids. Each acid is then superheated with water separately; xylene and sulphuric acid are formed. The xylene is then recovered by distillation.
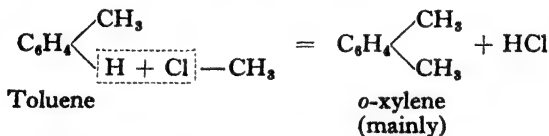
$$\underset{o\text{-},\ m\text{-},\ p\text{-xylene}}{C_6H_4(CH_3)_2} \xrightarrow{(H_2SO_4)} \underset{\substack{o\text{-},\ m\text{-xylene}\\ \text{sulphonic acid}\\ (p\text{- no action})}}{C_6H_3(CH_3)_2SO_3H} \xrightarrow{(NaOH)} \underset{\substack{\text{Sodium salts}\\ \text{separated}\\ (m\text{- salt more soluble})}}{C_6H_3(CH_3)_2SO_3Na} \xrightarrow{(HCl)}$$

$$\underset{\substack{o\text{- and }m\text{- acids}\\ \text{formed separately}}}{C_6H_3(CH_3)_2SO_3H} \xrightarrow{(HOH)} \underset{\substack{o\text{- and }m\text{- xylenes}\\ \text{obtained separately}}}{C_6H_4(CH_3)_2 + H_2SO_4}$$
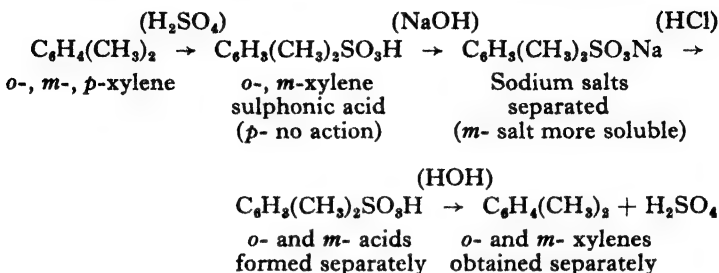
2. From toluene:

(*a*) By converting toluene into the three isomeric bromo-toluenes and treating these isomeric products separately with methyl iodide and sodium (Fittig's method):

$$\underset{o\text{-bromotoluene}}{C_6H_4 {\Huge<} \overset{CH_3}{\underset{\boxed{Br + Na} + \boxed{Na + I} CH_3}{}}} = \underset{o\text{-xylene}}{C_6H_4 {\Huge<} \overset{CH_3}{\underset{CH_3}{}}} + NaBr + NaI$$

(*b*) By the direct action of methyl chloride on toluene:

$$\underset{\text{Toluene}}{C_6H_4 {\Huge<} \overset{CH_3}{\underset{\boxed{H + Cl} —CH_3}{}}} = \underset{\substack{o\text{-xylene}\\ \text{(mainly)}}}{C_6H_4 {\Huge<} \overset{CH_3}{\underset{CH_3}{}}} + HCl$$

3.

Identification of the Xylenes.

Ortho-xylene, on oxidation with dilute nitric acid, is converted into ortho-toluic acid; further oxidation with nitric acid or potassium permanganate produces phthalic acid, which differs from the meta- and para-phthalic acid

isomers in forming an anhydride. This proves that the two methyl groups in the original substance are attached to adjacent carbon atoms.

o-xylene
(1 : 2)
(b. pt. 142° C.)

o-toluic acid
(1 : 2)
(m. pt. 105° C.)

o-phthalic acid
(1 : 2)
(m. pt. 213° C.)

Phthalic anhydride
(m. pt. 128° C.)
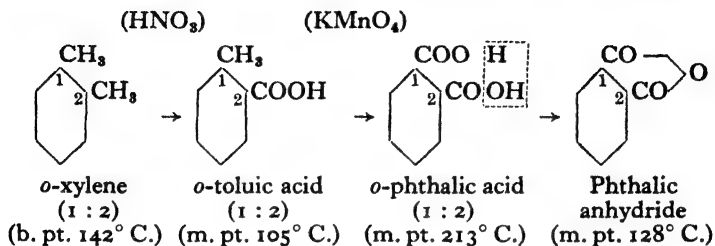
With chromic acid o-xylene is oxidized to carbon dioxide and water, whereas m- and p-xylene yield dicarboxylic acids.
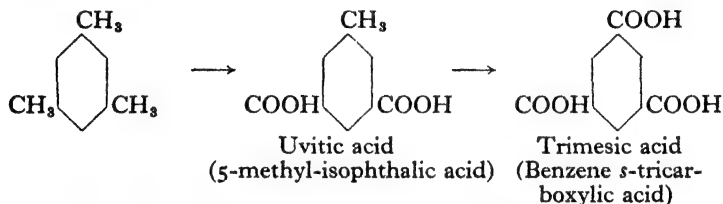

m-xylene(1 : 3)
(b. pt. 138° C.)

m-toluic acid
(1 : 3)
(m. pt. 111° C.)

m-phthalic acid or Isophthalic acid
(1 : 3)
(m. pt. about 300° C.)

p-xylene
(1 : 4)
(b. pt. 137° C.)

p-toluic acid
(1 : 4)
(m. pt. 180° C.)

p-phthalic acid or Terephthalic acid
(1 : 4)
(sublimes)
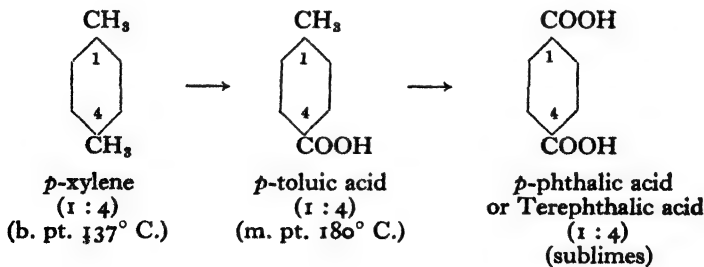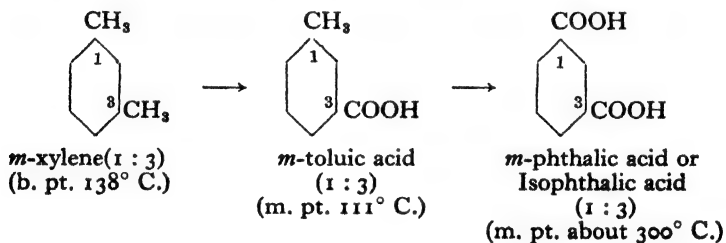
Meta-xylene is identified by its method of formation from symmetrical mesitylene. Mesitylene on oxidation is

converted into mesitylenic acid, which on distillation with soda lime yields *m*-xylene:

Mesitylene
(1 : 3 : 5 trimethyl
benzene)
(b. pt. 165° C.)

Mesitylenic acid
(1 : 3 : 5 dimethyl
benzoic acid)
(m. pt. 166° C.)

m-xylene
(1 : 3 dimethyl
benzene)
(b. pt. 138° C.)
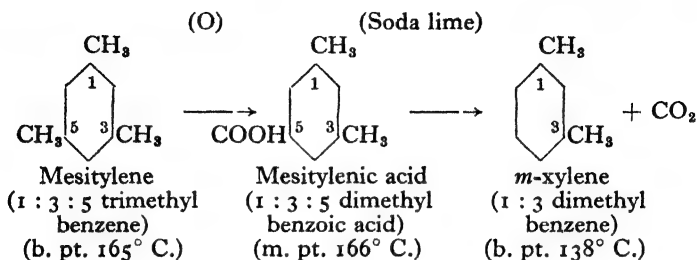
Further oxidation of mesitylene yields two other acids, as follows:

Uvitic acid
(5-methyl-isophthalic acid)

Trimesic acid
(Benzene *s*-tricar-
boxylic acid)

Uvitic acid and trimesic acid on distillation with soda lime decompose, liberating carbon dioxide and forming toluene and benzene respectively.

Para-xylene is identified by Körner's Method (p. 382), since it forms only one tri-derivative. It is formed from *p*-dibromobenzene, methyl iodide and sodium. On oxidation it yields terephthalic acid.

The three xylenes are all mobile, rather pleasant-smelling, inflammable liquids. They distil without decomposition, and are volatile in steam. The constitution of the xylenes is deduced from their methods of formation (cf. toluene).

Ethyl Benzene, Phenyl Ethane, $C_6H_5C_2H_5$, is isomeric with the xylenes. It occurs in coal tar, and may be obtained by general methods (cf. Toluene).

It is a colourless liquid, b. pt. 134° C. On oxidation with nitric or chromic acid it is converted into benzoic acid:

$$CH_2 \cdot CH_3 \quad\quad\quad COOH$$

Ethyl benzene $+ 3O_2 =$ Benzoic acid $+ CO_2 + 2H_2O$
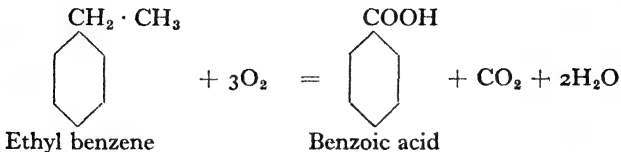
QUESTIONS

1. In what ways does chlorine react with organic compounds? Illustrate your answer by reference to its effects on (a) methane, (b) ethylene, (c) acetylene, (d) benzene, (e) toluene, (f) acetic acid. State the conditions under which the reactions occur.

(Oxford Higher School Cert.)

2. What are (a) benzine, (b) benzene, (c) petrol, (d) paraffin? How are ethane, ethylene, and benzene affected by (a) concentrated sulphuric acid, (b) bromine?

3. A mixture of benzol (benzene), petrol and alcohol makes a satisfactory motor spirit. What do you know of the properties, composition and sources of alcohol and benzene?

(Civil Service: Navy, Army and Air Force.)

4. The products of reaction are largely determined by the conditions of interaction. Illustrate this statement by reference to the reactions that take place between:

(a) Ethyl alcohol and sulphuric acid.
(b) Glycerol and oxalic acid.
(c) Chlorine and toluene.

5. For what purpose is sulphuric acid used in organic chemistry? Illustrate your answer by reference to its action on (a) ethyl alcohol, (b) methyl acetate, (c) ethylene, (d) sodium formate, (e) benzene. *(London Higher School Cert.)*

6. What are the characteristics and properties of (*a*) paraffins, (*b*) aromatic hydrocarbons. Illustrate your answer by reference to the properties and reactions of methane, benzene, and toluene.
(*Oxford Higher School Cert.*)

7. Suppose that you had four pure compounds whose molecular formulæ you had found to be C_3H_6O, C_3H_8O, C_7H_8 and C_2H_3N. Describe briefly *two* chemical reactions by which you could determine that the four compounds were respectively a ketone, a primary alcohol, an aromatic hydrocarbon and a nitrile. Suggest a structural formula for each of these compounds.
(*Cambridge Higher School Cert.*)

8. Write a brief account of the constitutional formulæ which have been assigned to benzene.

9. Give some account of the use of any two of the following inorganic substances in the synthesis of organic compounds: (*a*) sulphuric acid, (*b*) metallic sodium, (*c*) phosphorus pentachloride, (*d*) aluminium chloride. (*Phar. Chem. Qual.*)

10. Write an essay on the chemical structure of benzene.
(*Inst. of Patent Agents.*)

11. In what way is the strength of the valency bond between two atoms affected by the form of the molecule? Illustrate your answer by examples from organic chemistry.
(*Inst. of Patent Agents.*)

CHAPTER XVI

Aromatic Hydroxy-compounds

There are two classes of aromatic hydroxy-compounds

A. The **Phenols,**

B. The **Aromatic Alcohols,**

exemplified by:

OH   CH₂OH

Phenol   Benzyl alcohol
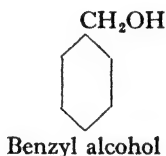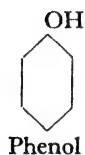
In the aromatic alcohols the hydroxyl group is present in the side chain, and is attached to a carbon atom which is not a member of the benzene ring.

In the phenols, the hydroxyl group is directly linked to a carbon atom of the benzene ring.

This difference of constitution is associated with a great difference in properties.

The aromatic alcohols are neutral substances and in most of their reactions they resemble the aliphatic alcohols; on oxidation, for instance, they are converted into aldehydes, ketones and acids. The phenols, on the other hand, are acid in character, and some of their derivatives are as strongly acid as the mineral acids. Phenols contain the tertiary alcohol group $=\!C\!-\!OH$ and in consequence they form neither aldehydes nor ketones on oxidation. Many phenols are found in coal tar.

Phenol, C_6H_5OH.

Occurrence.—Phenol, also known as *carbolic acid* from its acid properties, is found in coal tar, in small quantities in the human urine as phenyl hydrogen sulphate, and in the urine of herbivorous animals, e.g. the ox, in pyroligneous liquor and in bone oil.

It was discovered by Runge (1834) in coal tar.

Formation.

1. From coal tar. The carbolic oil fraction is allowed to stand; the naphthalene which it contains is deposited as crystals. These are separated, and the acid oil is then treated with a 10 per cent solution of sodium hydroxide; soluble sodium phenate is formed, leaving the other basic and neutral substances unattacked. This aqueous solution is then concentrated and decomposed either with sulphuric acid or by passing carbon dioxide through the solution; phenol separates as an oil and is purified by fractional distillation:

$$2C_6H_5 \cdot ONa + H_2SO_4 = 2C_6H_5OH + Na_2SO_4$$
$$\text{Sodium} \qquad\qquad\qquad \text{Phenol}$$
$$\text{phenate}$$
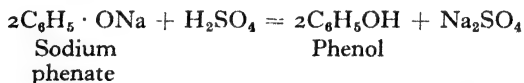
2. By treating salts of amino-compounds with nitrous acid in aqueous solution and then heating the solution until nitrogen is no longer evolved:

$$C_6H_5NH_2 \cdot HCl + HO \cdot NO = C_6H_5OH + N_2 + H_2O + HCl$$

It is thus possible to prepare phenols not only from the amino-compounds themselves but also indirectly from the corresponding nitro-derivatives and from the hydrocarbons, since these substances may be converted into amino-compounds:

$$C_6H_6 \rightarrow C_6H_5NO_2 \rightarrow C_6H_5NH_2 \rightarrow C_6H_5OH$$
$$\text{Benzene} \quad \text{Nitro-} \qquad \text{Aniline} \qquad \text{Phenol}$$
$$\text{benzene}$$
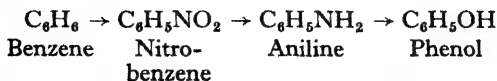
The conversion of an amino-compound into a phenol really takes place in two stages; at low temperatures the salt of the amino-compound is transformed into a diazonium salt (p. 470), but the latter decomposes when its aqueous solution is heated, yielding a phenol.

$$C_6H_5NH_2 \cdot HCl + HCl + KNO_2 = C_6H_5N:NCl + KCl + 2H_2O,$$
$$C_6H_5N_2Cl + HOH = C_6H_5OH + N_2 + HCl.$$
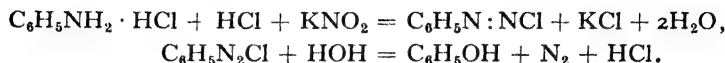
The nitrous acid is produced *in situ* by the action of a mineral acid on an alkali nitrite.

3. *Commercial Method.*—By fusing sulphonic acids or their salts with caustic alkalis:

$$C_6H_5 \cdot SO_2 \cdot OK + KOH = C_6H_5OH + K_2SO_3$$
Potassium
benzene
sulphonate

4. By distilling hydroxy-acids, e.g. salicylic acid, with lime:

$$C_6H_4(OH)COOH = C_6H_5OH + CO_2$$
Salicylic acid

This reaction is similar to that by which the hydrocarbons are prepared from the acids.

5. By oxidizing benzene with hydrogen peroxide in the presence of ferric sulphate:

$$C_6H_6 + H_2O_2 = C_6H_5OH + H_2O$$
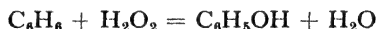
6. By Grignard's method (p. 485.)

Properties.—Pure phenol is a colourless crystalline hygroscopic solid, m. pt. 42° C., b. pt. 182° C. On exposure to light in the presence of air it turns pink. It has a burning taste, and is poisonous. It is sparingly soluble in cold water (1 in 15), and is volatile in steam. It has a characteristic smell, and a strong caustic action on the skin, which it rapidly blisters. It dissolves freely in most organic liquids, e.g. alcohol, ether.

Reactions.—1. Phenol behaves as an **acid,** reacting with alkalis to form salts known as *phenates*:

$$C_6H_5OH + NaOH = C_6H_5O \cdot Na + H_2O$$
<div align="center">Sodium
phenate</div>
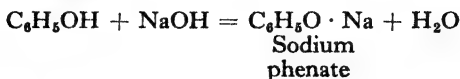
2. It reacts with dilute nitric acid to form ortho- and para- nitro-phenol:

$$C_6H_5OH + HONO_2 = C_6H_4OH \cdot NO_2 + H_2O$$
<div align="center">Nitro-phenol</div>

3. Nitric acid (sp. gr. 1·4) converts phenol into picric acid (trinitrophenol (p. 417)):

$$C_6H_5OH + 3HONO_2 = C_6H_2OH \cdot (NO_2)_3 + 3H_2O$$
<div align="center">Picric acid</div>
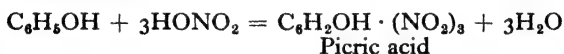
4. It reacts with concentrated sulphuric acid at a moderate temperature to form ortho- and para-phenol sulphonic acids:
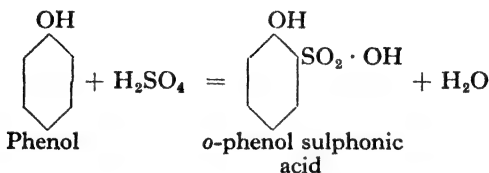
The ortho-acid is transformed into the para-acid when the aqueous solution is heated. The two acids may be separated by means of their potassium salts.

Ortho-phenol sulphonic acid is used as an antiseptic under the name of *aseptol* or *sozolic acid*.

5. It reacts with bromine water to form a white precipitate of tribromophenol (1 : 2 : 4 : 6):
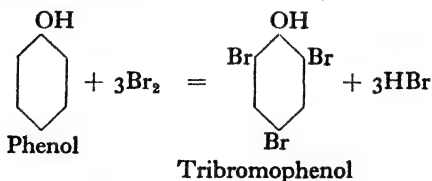
6. Phenol behaves as an **alcohol,** forming ethers, such as anisole, $C_6H_5O \cdot CH_3$.

$$C_6H_5OH + CH_3ONa = C_6H_5O \cdot Na + CH_3OH,$$
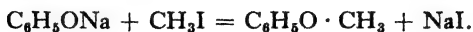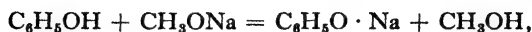
$$C_6H_5ONa + CH_3I = C_6H_5O \cdot CH_3 + NaI.$$
Anisole

7. It forms esters, such as phenyl acetate (methyl benzoate), $C_6H_5O \cdot CO \cdot CH_3$ (b. pt. 199° C.), when acted on by an acid chloride, either alone or in the presence of an alkali:

| Phenol | Acetyl chloride | Methyl benzoate |
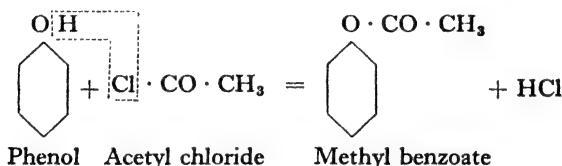
Phenol also forms thio-compounds, such as thio-phenol, C_6H_5SH.

8. When distilled with zinc dust it is reduced to benzene:

$$C_6H_5OH + Zn = ZnO + C_6H_6$$
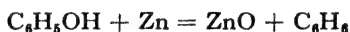
9. The hydroxyl group is displaced by halogens when phenol is treated with phosphorus halides:

$$C_6H_5OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl$$

10. *Tiemann-Reimer Reaction.*—Phenol reacts with a mixture of carbon tetrachloride and sodium hydroxide on warming, to form a di-sodium salt of salicylic acid; substitution takes place in the ortho-position:
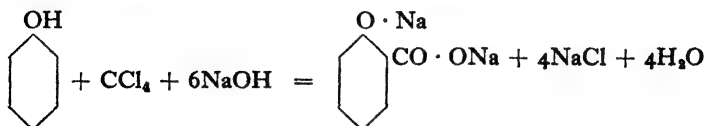
This salt on treatment with sulphuric acid yields salicylic acid (p. 430):

$$\text{Di-sodium salicylate} + H_2SO_4 = \text{Salicylic acid} + Na_2SO_4$$

O · Na / CO · ONa + H_2SO_4 = OH / COOH + Na_2SO_4

·Di-sodium
salicylate

Salicylic acid
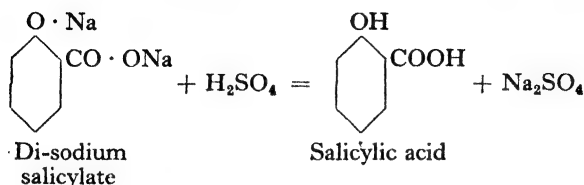
The phenols are comparable with tertiary alcohols only, since they do not yield acids and ketones containing the same number of carbon atoms.

Phenol also acts as an aromatic compound. It cannot be prepared by the action of sodium hydroxide upon chloro-, bromo-, or iodo-benzene, as is the case with aliphatic alcohols. The —OH group is distinctly acidic. Phenol gives *Liebermann's Reaction*: Phenol is first dissolved in concentrated sulphuric acid and a crystal of sodium nitrite added. When the liquid is poured into sodium hydroxide solution the colour turns to blue or green.

Tests for Phenol are given on p. 534.

Uses.—It is a powerful germicide, and is used as a disinfectant although it is poisonous. A 3 per cent solution is used for washing wounds or cleansing the skin. It is used for the manufacture of salicylic acid, picric acid, phenacetin (*p*-acetaminophenyl ether),

$$C_2H_5O \cdot C_6H_4NHCO \cdot CH_3$$

and certain drugs and dyes.

Phenol condenses with formaldehyde in alkaline solution, giving a liquid which is converted into a hard solid (bakelite) when it is heated under pressure. Bakelite is used as a substitute for celluloid, shellac, rubber, &c., and for many other commercial purposes.

## Picric Acid, Trinitrophenol, $C_6H_2OH \cdot (NO_2)_3$.

Formation.

1. By dissolving phenol in concentrated sulphuric acid and treating the resulting phenol sulphonic acids with nitric acid:

Phenol sulphonic acid   Trinitrophenol
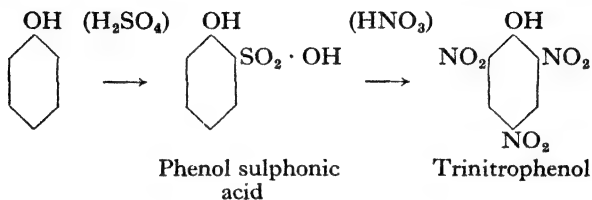
For practical details, see p. 591.

2. By the oxidation of symmetrical trinitrobenzene with potassium ferricyanide:

Symmetrical trinitrobenzene   Picric acid
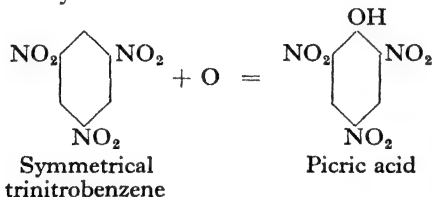
This reaction establishes the symmetrical structure of picric acid.

Properties.—Picric acid is obtained as yellow crystals, m. pt. 122° C. It has an extremely bitter taste, hence its name, from the Greek πικρός (*pikros*), bitter. It can be crystallized from hot water. It is a strong acid, owing to the influence of the three nitro-groups on the hydroxyl group. It differs from phenol in that it can decompose carbonates to form well-defined salts, known as *picrates*, and can react with phosphorus pentachloride to form picryl chloride, $C_6H_2(NO_2)_3Cl$. This chloride can be hydrolysed to re-form picric acid, a reaction similar to that of an

aliphatic chloride. Picric acid also reacts with ammonia to form picramide, $C_6H_2(NO_2)_3 \cdot NH_2$.

With bleaching powder it forms chloropicrin, $CCl_3 \cdot NO_2$, one of the " poison gases " used in war.

Chloropicrin is a heavy liquid; b. pt. $112°$. It has an extremely suffocating smell.

Picric acid is used as a high explosive under the name of lyddite, and also as a dye.

## Benzyl alcohol, Phenyl carbinol, $C_6H_5 \cdot CH_2 \cdot OH$.

Occurrence.—Benzyl alcohol occurs in the form of its esters in essential oils of flowers, such as the oils of tuberose, cloves, hyacinth and jasmine. It is also found in Tolu and Peru balsams.

Formation.

1. By boiling benzyl chloride with either potassium carbonate solution or lead oxide in aqueous suspension:

$$2C_6H_5 \cdot CH_2Cl + K_2CO_3 + H_2O = 2C_6H_5 \cdot CH_2OH + 2KCl + CO_2$$

2. *Cannizzaro's Reaction.*—By the action of caustic alkalis on benzaldehyde; two molecules of the aldehyde are transformed by mutual oxidation and reduction into one molecule each of benzyl alcohol and a benzoate:

Benzaldehyde + KOH + = Benzyl alcohol + Potassium benzoate
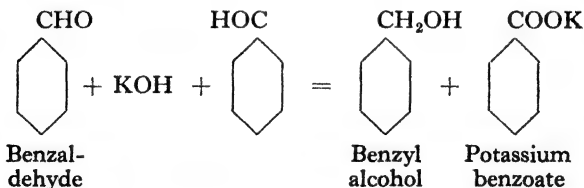
3. By reducing benzaldehyde with sodium amalgam and water:

$$C_6H_5CHO + 2H = C_6H_5 \cdot CH_2 \cdot OH$$

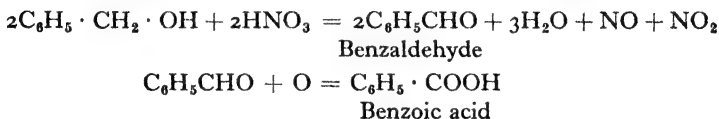*Properties.*—Colourless oil, b. pt. $206°$ C. It is sparingly

soluble in water, but readily soluble in organic liquids. It resembles the aliphatic alcohols in its chemical properties.

Reactions.—1. With sodium it forms sodium benzoxide, $C_6H_5 \cdot CH_2 \cdot ONa$, hydrogen being liberated at the same time. (Cf. aliphatic primary alcohols.)

2. With acetyl chloride it forms benzyl acetate, $C_6H_5 \cdot CH_2 \cdot O \cdot CO \cdot CH_3$. Other esters are also formed with concentrated acids or anhydrides.

3. With phosphorus pentachloride it forms benzyl chloride, $C_6H_5 \cdot CH_2Cl$.

4. With chromic acid or nitric acid it forms first benzaldehyde, $C_6H_5 \cdot CHO$, and then benzoic acid, $C_6H_5 \cdot COOH$:

$$2C_6H_5 \cdot CH_2 \cdot OH + 2HNO_3 = 2C_6H_5CHO + 3H_2O + NO + NO_2$$
<div align="center">Benzaldehyde</div>

$$C_6H_5CHO + O = C_6H_5 \cdot COOH$$
<div align="center">Benzoic acid</div>

This oxidation reaction indicates that benzyl alcohol is a primary alcohol.

*Uses.*—In the manufacture of perfumes and in medicine.

The **Cresols** or **Hydroxy-toluenes,** $C_6H_4 \cdot OH \cdot CH_3$, are isomeric with benzyl alcohol. They are found in coal tar and resemble phenol in most of their properties, except that they are not oxidized by chromic acid; that is, the hydroxy-group protects the methyl group (toluene is oxidized slowly to benzoic acid). The cresols are represented as follows:
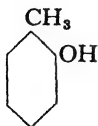
o-cresol
(m. pt. 31° C.,
b. pt. 190° C.,
sp. gr. 1·052)
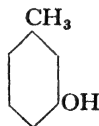
m-cresol
(m. pt. 3° C.,
b. pt. 202° C.,
sp. gr. 1·05)
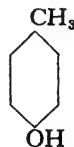
*p*-cresol
(m. pt. 35° C.,
b. pt. 201° C.,
sp. gr. 1·034)

Polyhydric Phenols.

A. **Dihydric Phenols** are similar to phenol in many of their properties, but can be oxidized much more rapidly. Many of the polyhydric phenols are strong reducing agents. Quinol (hydroquinone) is used as a developer in photography. Resorcinol can be used as an antiseptic, and for the preparation of fluorescein and eosin dyes. They may be represented as follows:
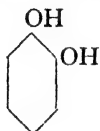
Catechol
(o-dihydroxy-
benzene)
m. pt. 104° C.,
b. pt. 245° C.
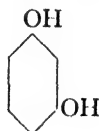
Resorcinol
(m-dihydroxy-
benzene)
m. pt. 118° C.,
b. pt. 276° C.
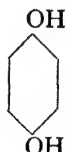
Quinol or hydro-
quinone
(p-dihydroxy-
benzene)
m. pt. 169° C.
b. pt. 285° C.

B. **Trihydric Phenols** have properties similar to those of the dihydric phenols. Pyrogallol is used as a developer in photography. Alkaline pyrogallol, also known as sodium pyrogallate, is used in gas analysis for the estimation of oxygen. The three isomers are represented as follows:
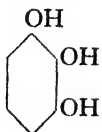
Pyrogallol
(1 : 2 : 3 trihydroxy-
benzene)
m. pt. 133° C.
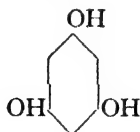
Phloroglucinol
(1 : 3 : 5 trihydroxy-
benzene)
m. pt. 218° C.
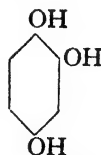
Hydroxy-quinol
(1 : 2 : 4 trihydroxy-
benzene
m. pt. 140° C.

QUESTIONS

1. Give two synthetic methods for the preparation of phenol. What is the action of the following reagents on phenol: (*a*) caustic soda, (*b*) bromine, (*c*) nitric acid, (*d*) sulphuric acid, (*e*) acetyl chloride?   (*Phar. Chem. Qual.*)

2. Describe how you would prepare a pure sample of nitro-benzene from benzene. How may nitrobenzene be converted to phenol?

Outline another method by which phenol could be prepared from benzene.   (*Cambridge Higher School Cert.*)

3. Describe two methods of making phenol from benzene. Discuss, by comparing the properties and structure of phenol with those of aliphatic alcohols, whether phenol should be classed as an alcohol.   (*Oxford Higher School Cert.*)

4. What is meant by (*a*) an unsaturated compound, (*b*) isomeric compounds?

(*a*) Name and give the structural formulæ of two unsaturated compounds, choosing examples of different chemical type. Describe two reactions for each compound which demonstrate the unsaturation.

(*b*) Name and give the structural formulæ of two pairs of isomeric compounds. Describe in each case two reactions which would serve to distinguish between the isomers.

(*Cambridge Higher School Cert.*)

5. How may phenol be separated from coal tar? Explain the reactions involved in the conversion of phenol into (*a*) salicylic acid, (*b*) phenolphthalein, (*c*) benzene, and (*d*) picric acid.

(*Chemists and Druggists Qual.*)

6. How would you demonstrate the presence of (*a*) alcoholic, (*b*) phenolic hydroxyl groups in an organic compound, and how could their number be determined?   (*Phar. Chem. Qual.*)

Benzoic Acid and its Derivatives

A. ACIDS

Benzoic Acid, C_6H_5COOH.

Benzoic acid was first discovered in 1608 in gum benzoin. Scheele (1785) first prepared the acid from urine.

Occurrence.—Benzoic acid occurs in gum benzoin and other resins; in the urine of herbivorous animals as hippuric acid (benzoyl glycine); in Peru and Tolu balsams as the benzyl ester, and in cranberries.

Formation.

1. By subliming gum benzoin in iron vessels; the benzoic acid sublimate is purified by recrystallization from hot water.

2. By hydrolysing hippuric acid, obtained from the urine of horses and other ruminants, with hydrochloric acid (see p. 250):

3. *Commercial Methods.*

(*a*) By oxidizing benzyl chloride with 60 per cent nitric acid:

$$C_6H_5 \cdot CH_2Cl + 2HNO_3 = C_6H_5COOH + HCl + H_2O + N_2O_3$$
Benzyl chloride
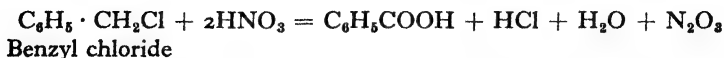
(*b*) By heating benzotrichloride (p. 405) with milk of lime

and decomposing the lime salt with mineral acid; benzoic acid crystallizes out:

$$2C_6H_5CCl_3 + 4Ca(OH)_2 = (C_6H_5COO)_2Ca + 3CaCl_2 + 4H_2O$$

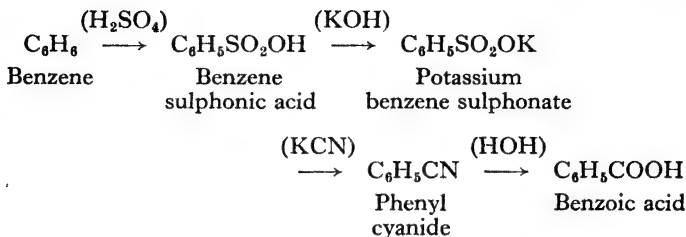Benzo-   Calcium
trichloride   benzoate

$$(C_6H_5COO)_2Ca + 2HCl = 2C_6H_5COOH + CaCl_2$$

(c) By heating calcium phthalate with lime at about 350° C. and decomposing the calcium salt with mineral acid:

$$2C_6H_4(COO)_2Ca + Ca(OH)_2 = (C_6H_5COO)_2Ca + 2CaCO_3$$

Calcium phthalate

4. By oxidizing toluene, benzyl alcohol, or benzaldehyde and other aromatic compounds containing one side chain with nitric acid, or by boiling with acidified potassium permanganate solution in the case of toluene and with alkaline permanganate in the case of other aromatic compounds:

$$C_6H_5 \cdot CH_3 + 2KMnO_4 = C_6H_5COOK + KOH + 2MnO_2 + H_2O$$

Toluene   (acid)   Potassium
                        benzoate

$$2C_6H_5CH_2Cl + Na_2CO_3 + H_2O = 2C_6H_5CH_2OH + 2NaCl + CO_2$$

Benzyl chloride   Benzyl alcohol

$$3C_6H_5CH_2OH + 4KMnO_4 \text{ (alkaline)}$$

Benzyl alcohol $$= 3C_6H_5COOK + KOH + 4MnO_2 + 4H_2O$$

The potassium salt formed is decomposed by mineral acid.

For practical details, see p. 590.

5. By hydrolysing phenyl cyanide (benzonitrile) with sodium hydroxide or 25 per cent sulphuric acid:

$$C_6H_5CN + 2HOH = C_6H_5COOH + NH_3$$

Benzonitrile

This method is important in the synthesis of benzoic acid from benzene:

$$C_6H_6 \xrightarrow{(H_2SO_4)} C_6H_5SO_2OH \xrightarrow{(KOH)} C_6H_5SO_2OK$$

Benzene   Benzene   Potassium
sulphonic acid   benzene sulphonate

$$\xrightarrow{(KCN)} C_6H_5CN \xrightarrow{(HOH)} C_6H_5COOH$$

Phenyl   Benzoic acid
cyanide

6. By Grignard's method (p. 485).

Properties.—Soft white crystalline substance, m. pt. 121° C., b. pt. 249° C. It is soluble in hot water but sparingly soluble in cold water; hence it can be recrystallized from hot water. It is soluble in alcohol, ether, and most organic solvents. It sublimes readily, and hence can be purified by sublimation. Its vapour has a pleasant smell, but affects the membranes of the nose and throat, producing coughing. It behaves in most respects like the fatty acids.

Reactions.—1. When acted upon by phosphorus pentachloride it forms benzoyl chloride (p. 427):

$$C_6H_5COOH + PCl_5 = C_6H_5COCl + HCl + POCl_3$$

Benzoyl
chloride
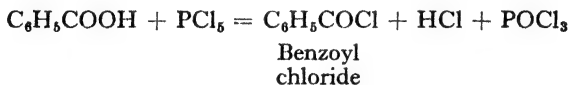
This reaction indicates that benzoic acid contains a hydroxyl —OH group.

2. When heated with soda lime it is decomposed into benzene and carbon dioxide:

$$C_6H_5COOH = C_6H_6 + CO_2$$

Benzene
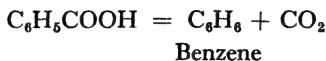
3. It behaves as an acid, reacting with bases to form

well-defined salts known as *benzoates*. Most of these salts
are soluble in water, e.g.

$$\left.\begin{array}{c} C_6H_5COO \\ \\ C_6H_5COO \end{array}\right\rangle Ca \cdot 3H_2O, \text{ Calcium benzoate}$$
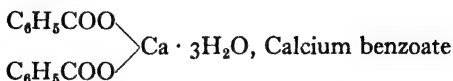
It is a stronger acid than acetic acid, owing to the presence
of the phenyl —C_6H_5 group.

Ferric benzoate, $Fe(C_6H_5COO)_3$, is obtained as a brown
precipitate when ferric chloride is added to a neutral solution
of a soluble benzoate.

4. It reacts with alcohols in the presence of a little mineral
acid to form esters:

$$C_6H_5COOH + C_2H_5OH = C_6H_5COOC_2H_5 + H_2O$$
Benzoic acid   Ethyl alcohol   Ethyl benzoate
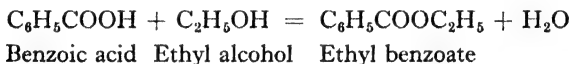
These esters can be readily saponified with boiling alcoholic
potash solution:

$$C_6H_5COOC_2H_5 + KOH = C_6H_5COOK + C_2H_5OH$$

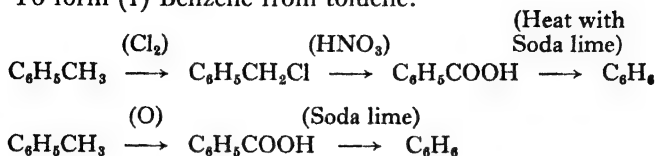Ethyl benzoate is a pleasant-smelling oil, b. pt. 213° C.

5. It can be chlorinated, brominated, nitrated, sul-
phonated, &c. Substitution takes place in the benzene
nucleus, usually in the meta-position:

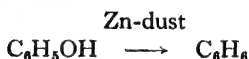Benzoic acid   *m*-bromobenzoic acid
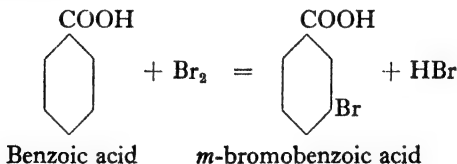
Uses.—Benzoic acid and some of its salts are used in
medicine. The acid possesses antiseptic properties. It is
also used in the manufacture of aniline blue.
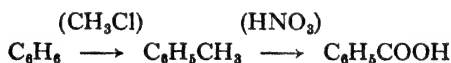
Summary

To form (1) Benzene from toluene:

$$C_6H_5CH_3 \xrightarrow{(Cl_2)} C_6H_5CH_2Cl \xrightarrow{(HNO_3)} C_6H_5COOH \xrightarrow{\substack{\text{(Heat with} \\ \text{Soda lime)}}} C_6H_6$$

$$C_6H_5CH_3 \xrightarrow{(O)} C_6H_5COOH \xrightarrow{\text{(Soda lime)}} C_6H_6$$

(2) Benzene from phenol:

$$C_6H_5OH \xrightarrow{\text{Zn-dust}} C_6H_6$$

(3) Benzene from benzoic acid:

$$C_6H_5COOH \longrightarrow (C_6H_5COO)_2Ca \xrightarrow{\text{(lime)}} C_6H_6$$

(4) Toluene from benzene:

$$C_6H_6 \text{ (Friedel-Crafts } (CH_3Cl)) \longrightarrow C_6H_5CH_3$$

(5) Benzoic acid from benzene or toluene:

$$C_6H_6 \xrightarrow{(CH_3Cl)} C_6H_5CH_3 \xrightarrow{(HNO_3)} C_6H_5COOH$$

(6) Phenol from benzene or aniline:

$$C_6H_6 \rightarrow C_6H_5NO_2 \rightarrow C_6H_5NH_2 \rightarrow C_6H_5N:N\cdot Cl \rightarrow C_6H_5OH$$

(7) Phenol from salicylic acid:

$$C_6H_4OH\cdot COOH \xrightarrow{\text{(Soda-lime)}} C_6H_5OH$$
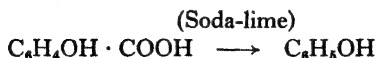
(8) Benzene from salicylic acid:

$$C_6H_4\cdot OH\cdot COOH \xrightarrow{\text{(Soda lime)}} C_6H_5OH \xrightarrow{\text{(Zn-dust)}} C_6H_6$$

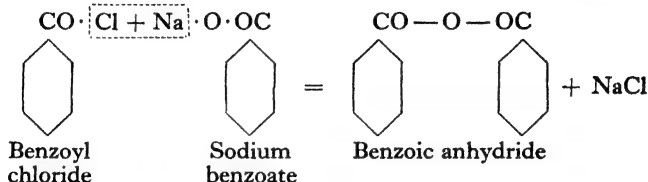**Benzoic Anhydride,** $\begin{matrix} C_6H_5 \cdot CO \\ C_6H_5 \cdot CO \end{matrix} \Big\rangle O.$
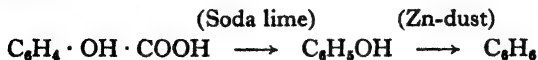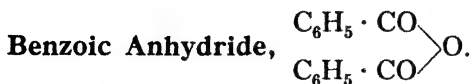
This anhydride is prepared by heating a mixture of benzoyl chloride and dry sodium benzoate in equimolecular proportions:

Benzoyl chloride   Sodium benzoate   Benzoic anhydride   + NaCl

It is a crystalline solid, m. pt. 42° C., b. pt. 360° C. It closely resembles acetic anhydride in its chemical properties. It combines with alcohols and phenols, like benzoyl chloride.

It is used for the detection of hydroxy- and amino-compounds. It is slowly decomposed by boiling water.

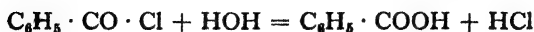**Benzoyl Chloride,** $C_6H_5 \cdot CO \cdot Cl.$

This compound is prepared by the action of phosphorus pentachloride on benzoic acid. Five per cent more than the molecular proportion of phosphorus pentachloride required by the equation must be added:
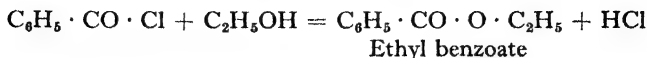
$$C_6H_5 \cdot COOH + PCl_5 = C_6H_5 \cdot CO \cdot Cl + POCl_3 + HCl$$

The benzoyl chloride is separated from the phosphorus oxychloride by distillation; the latter, which boils at 107° C., distils over first.

Properties.—Benzoyl chloride is a colourless fuming liquid, b. pt. 197° C. It is similar to acetyl chloride in chemical properties.

Reactions.—1. It is hydrolysed slowly by water to benzoic acid:

$$C_6H_5 \cdot CO \cdot Cl + HOH = C_6H_5 \cdot COOH + HCl$$

2. It reacts with alcohols to form esters:

$$C_6H_5 \cdot CO \cdot Cl + C_2H_5OH = C_6H_5 \cdot CO \cdot O \cdot C_2H_5 + HCl$$
Ethyl benzoate

3. It forms an amide with ammonia:

$$C_6H_5 \cdot CO \cdot Cl + 2NH_3 = C_6H_5 \cdot CO \cdot NH_2 + NH_4Cl$$
Benzamide

Benzamide, $C_6H_5 \cdot CO \cdot NH_2$.

Formation.

1. By heating ethyl benzoate with ammonia:

$$C_6H_5 \cdot COOC_2H_5 + NH_3 = C_6H_5 \cdot CO \cdot NH_2 + C_2H_5OH$$
Ethyl benzoate   Benzamide

2. By the action of benzoyl chloride on ammonium carbamate or on ammonia:

$$C_6H_5 \cdot CO \cdot Cl + NH_4 \cdot NH_2CO_2 = C_6H_5 \cdot CO \cdot NH_2 + NH_4Cl + CO_2$$
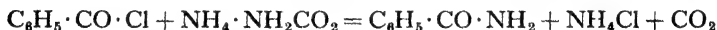
Properties.—White solid, m. pt. 128° C., b. pt. 290° C.; sparingly soluble in cold water but soluble in hot water.

Reactions.—1. When heated with caustic alkalis it is converted into sodium benzoate and ammonia is liberated:

$$C_6H_5 \cdot CO \cdot NH_2 + NaOH = C_6H_5 \cdot CO \cdot ONa + NH_3$$
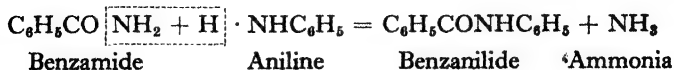Benzamide   Sodium benzoate

2. Heated with phosphorus pentoxide or pentachloride it is converted into benzonitrile (see below):

3. It gives an acid on hydrolysis, like other amides:

$$C_6H_5CONH_2 + HOH = C_6H_5COOH + NH_3$$
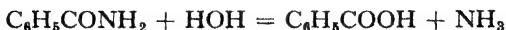
4. When heated with aniline it forms benzanilide and ammonia:

$$C_6H_5CO \underbrace{NH_2 + H} \cdot NHC_6H_5 = C_6H_5CONHC_6H_5 + NH_3$$
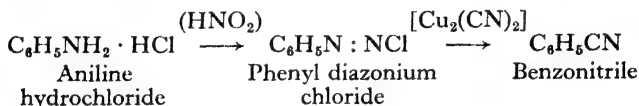Benzamide   Aniline   Benzanilide   ʻAmmonia

Benzonitrile, Phenyl Cyanide, C_6H_5CN.

Formation.

1. By distilling benzoic acid with ammonium or potassium thiocyanate:

$$2C_6H_5COOH + NH_4CNS = C_6H_5CN + C_6H_5COONH_4 + CO_2 + H_2S$$
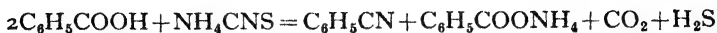
2. *Sandmeyer's reaction*: By diazotizing aniline and distilling the phenyl diazonium chloride with cuprous cyanide:

$$C_6H_5NH_2 \cdot HCl \xrightarrow{(HNO_2)} C_6H_5N : NCl \xrightarrow{[Cu_2(CN)_2]} C_6H_5CN$$

Aniline   Phenyl diazonium   Benzonitrile
hydrochloride   chloride

3. By the action of phosphorus pentachloride on benzamide:

$$C_6H_5CONH_2 + PCl_5 = C_6H_5CN + POCl_3 + 2HCl$$

Properties.—Colourless oily liquid, b. pt. 190° C. Characteristic smell, similar to that of benzaldehyde. Its reactions resemble those of aliphatic nitriles.
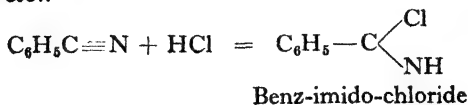
Reactions.—1. On hydrolysis with acids or alkalis it is converted to benzoic acid:

$$C_6H_5CN + 2HOH = C_6H_5COOH + NH_3$$

2. On reduction (by sodium and alcohol) it is converted to a primary amine:

$$C_6H_5CN + 2H_2 = C_6H_5CH_2NH_2$$
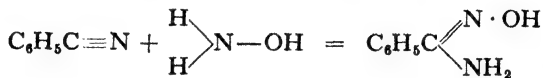Benzylamine
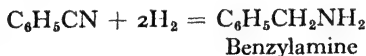
3. It combines with hydrogen chloride and other halogen hydrides to form additive compounds known as imidochlorides, &c.:

$$C_6H_5C \equiv N + HCl = C_6H_5 - C{\begin{smallmatrix} Cl \\ NH \end{smallmatrix}}$$
Benz-imido-chloride

4. It reacts with ammonia bases to form amidines:

$$C_6H_5C \equiv\!\!\equiv N + \begin{array}{c} H \\ \\ H \end{array}\!\!\!\!\searrow\!\!\nearrow NC_6H_5 \;=\; C_6H_5-C\!\!\!\begin{array}{c} \nearrow N \cdot H \\ \\ \searrow NH \cdot C_6H_5 \end{array}$$
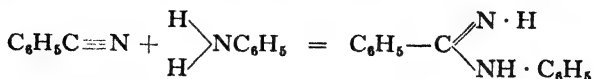
5. It reacts with hydroxylamine to form an amidoxime:

$$C_6H_5C \equiv\!\!\equiv N + \begin{array}{c} H \\ \\ H \end{array}\!\!\!\!\searrow\!\!\nearrow N\!-\!OH \;=\; C_6H_5C\!\!\!\begin{array}{c} \nearrow N \cdot OH \\ \\ \searrow NH_2 \end{array}$$

Salicylic Acid, *o*-Hydroxy-benzoic Acid, $C_6H_4 \cdot OH \cdot COOH$.

Occurrence.—In oil of wintergreen as the methyl ester $C_6H_4OHCOOCH_3$, which is prepared from the leaves of *Gaultheria procumbens.* Its name is derived from the glucoside salicin, found in the bark and leaves of the willow (*Salix*).
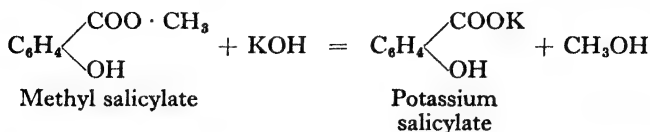
Formation.

1. *Commercial Method.*

(a) *Kolbe's Method*: by heating dry sodium phenate with carbon dioxide in an autoclave under 10 atmospheres at 100°–145° C. The carbon dioxide is rapidly absorbed to form sodium phenyl carbonate, which undergoes intra-molecular change into sodium salicylate.

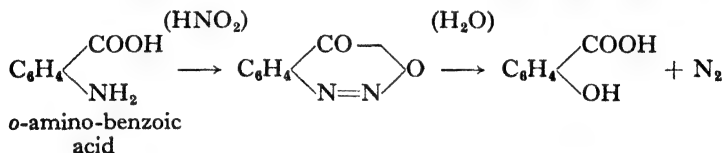| Sodium phenate | | Sodium phenyl carbonate | Sodium salicylate |
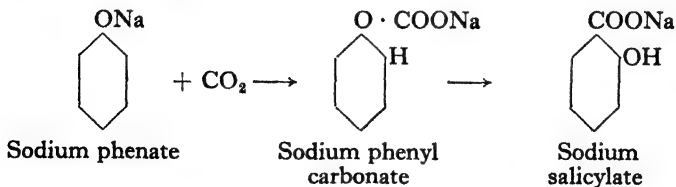
The acid is obtained from this salt by treatment with dilute mineral acid.

(*b*) For pharmaceutical purposes; by the saponification of oil of wintergreen (methyl salicylate):

$$C_6H_4\begin{smallmatrix}COO \cdot CH_3 \\ \\ OH\end{smallmatrix} + KOH = C_6H_4\begin{smallmatrix}COOK \\ \\ OH\end{smallmatrix} + CH_3OH$$

Methyl salicylate   Potassium
   salicylate

The acid is liberated from the potassium salt by treatment with mineral acid.

2. By the diazotization of *o*-amino-benzoic acid, giving the inner diazonium salt, which is then boiled with water:

$$C_6H_4\begin{smallmatrix}COOH \\ \\ NH_2\end{smallmatrix} \xrightarrow{(HNO_2)} C_6H_4\begin{smallmatrix}CO \\ \\ N=N\end{smallmatrix}O \xrightarrow{(H_2O)} C_6H_4\begin{smallmatrix}COOH \\ \\ OH\end{smallmatrix} + N_2$$

o-amino-benzoic
acid

3. By the oxidation of salicylaldehyde or salicyl alcohol with chromic acid:

Salicylaldehyde or   Salicylic acid
o-hydroxy-benzaldehyde
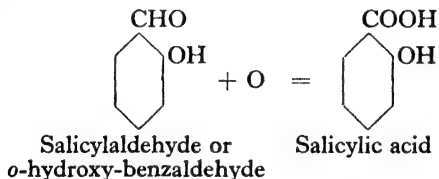
4. By the Tiemann-Reimer reaction (p. 415) i.e. heating phenol with carbon tetrachloride and alcoholic potash:

$$C_6H_5 \cdot OH + CCl_4 + 6KOH = C_6H_4\begin{smallmatrix}OK \\ \\ COOK\end{smallmatrix} + 4KCl + 4H_2O$$
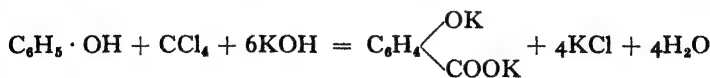
This reaction is important, as substitution here takes place in the ortho- position.

An extension of this reaction is used to introduce an aldehyde —CHO group into phenols by employing chloroform in place of carbon tetrachloride. The reaction is

carried out in alkaline aqueous solution. Phenol, for example, gives salicylaldehyde, which on oxidation gives salicylic acid:
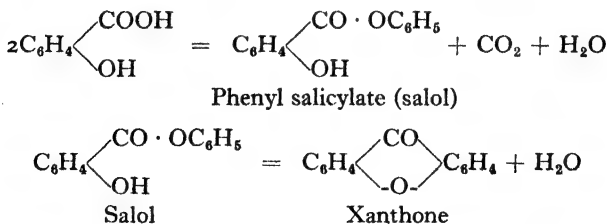
$$\text{(CHCl}_3\text{)}$$

$$C_6H_5OH \longrightarrow C_6H_4{<}^{CHCl_2}_{OH} \longrightarrow$$

Phenol   Dichlorocresol

$$\text{(2NaOH)}$$

$$\longrightarrow C_6H_4{<}^{CH(OH)_2}_{OH} \longrightarrow C_6H_4{<}^{CHO}_{OH}$$

Salicylaldehyde
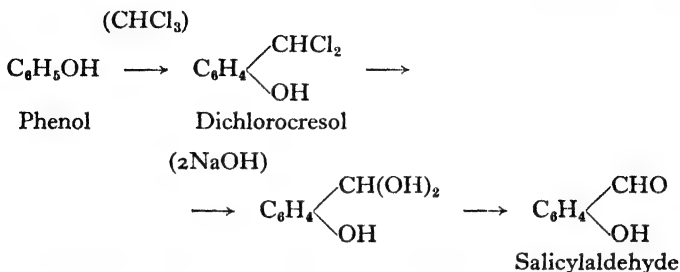
Properties.—White crystalline substance, m. pt. 155° C. It is sparingly soluble in cold water, and can be crystallized from hot water in needles. It acts as a phenol as well as an aromatic acid.

Reactions.—1. When heated with soda lime, it decomposes into phenol and carbon dioxide:

$$C_6H_4{<}^{COOH}_{OH} = C_6H_5OH + CO_2$$
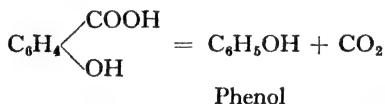
Phenol

2. By direct heating it is converted into phenyl salicylate (salol) and xanthone:

$$2C_6H_4{<}^{COOH}_{OH} = C_6H_4{<}^{CO \cdot OC_6H_5}_{OH} + CO_2 + H_2O$$
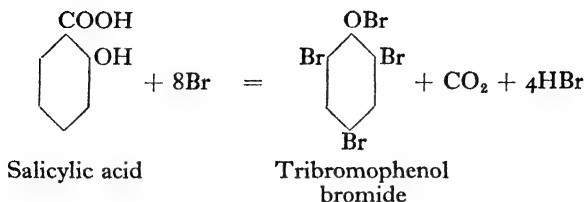
Phenyl salicylate (salol)

$$C_6H_4{<}^{CO \cdot OC_6H_5}_{OH} = C_6H_4{<}^{CO}_{-O-}{>}C_6H_4 + H_2O$$

Salol   Xanthone

3. With ferric chloride in neutral solution it gives a violet-blue coloration, like phenol.

4. With bromine water it forms tribromophenol bromide:

| Salicylic acid | Tribromophenol bromide |

$$COOH \cdot OH \cdot C_6H_? + 8Br = OBr, Br, Br, Br + CO_2 + 4HBr$$
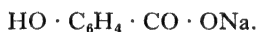
This reaction is used for the quantitative estimation of salicylic acid.

5. As an acid it forms salts known as *salicylates*. With sodium hydroxide it forms the di-sodium salt

$$NaO \cdot C_6H_4 \cdot CO \cdot ONa.$$
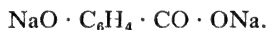
With sodium carbonate it forms the mono-sodium salt

$$HO \cdot C_6H_4 \cdot CO \cdot ONa.$$

The phenolic group is too weak an acid to decompose the carbonate.

When salicylic acid is boiled with milk of lime the hydrogen atoms from both the hydroxyl group and the carboxyl group are displaced to form calcium salicylate:

$$C_6H_4 \begin{matrix} COO \\ O \end{matrix} Ca.$$
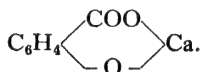
6. With methyl alcohol and sulphuric acid it undergoes esterification, forming the monomethyl ester, oil of wintergreen, $HO \cdot C_6H_4 \cdot CO \cdot OCH_3$.

7. With acetyl chloride it forms acetylsalicylic acid (aspirin):

$$C_6H_4 \begin{matrix} COOH \\ OH \end{matrix} + CH_3 \cdot COCl = C_6H_4 \begin{matrix} COOH \\ O \cdot CO \cdot CH_3 \end{matrix} + HCl$$
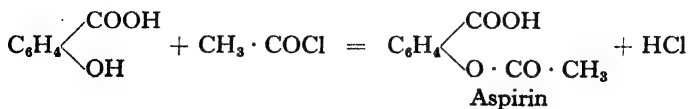
Aspirin

Uses.—The free acid is a powerful antiseptic, preventing putrefaction and fermentation, and can be used for preserving foods. It is used in medicine in cases of rheumatism and as an antipyretic. From it synthetic remedies, such as aspirin and salol, are prepared, and it is also used in the preparation of azo-dyes. The methyl ester is used for flavouring confectionery and chewing gum, and in perfumery.

B. Aldehydes

There are two classes of aromatic aldehydes:

(*a*) those which contain the —CHO group in the side chain;

(*b*) those which contain the —CHO group in the nucleus.

Compounds of the first class have properties similar to those of the aliphatic aldehydes and will not be dealt with in this book.

Benzaldehyde will be discussed as an illustration of the second class.

Benzaldehyde, Oil of Bitter Almonds, $C_6H_5 \cdot CHO$.

Occurrence.—In bitter almonds, cherry kernels, and cherry laurel leaves.

Formation.

1. By the hydrolysis of bitter almonds, which contain the glucoside amygdalin $C_{20}H_{27}NO_{11}$. The hydrolysis is caused by the enzyme *emulsin* which is present in the almonds, or by boiling with dilute acids.

$$C_6H_5 \cdot CH{\diagup}^{CN}_{\diagdown O \cdot C_{12}H_{21}O_{10}} + 2HOH$$

Amygdalin

$$= C_6H_5 \cdot CHO + HCN + 2C_6H_{12}O_6$$

Benzaldehyde   Glucose
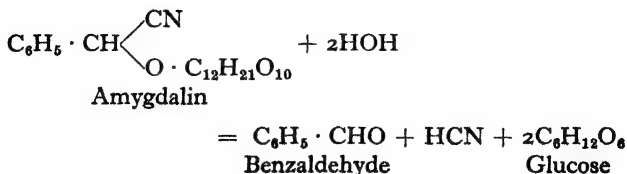
2. By the distillation of a mixture of calcium benzoate and calcium formate:

$$\begin{matrix} C_6H_5CO \cdot O \\ C_6H_5CO \cdot O \end{matrix} \Big\rangle Ca + Ca \Big\langle \begin{matrix} OOC \cdot H \\ OOC \cdot H \end{matrix} = 2C_6H_5 \cdot CHO + 2CaCO_3$$
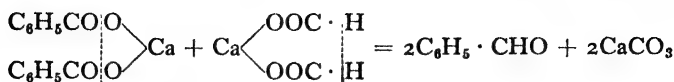
3. By reducing benzoyl chloride with nascent hydrogen:

$$C_6H_5CO \cdot Cl + 2H = C_6H_5 \cdot CHO + HCl$$
Benzoyl chloride

4. *Commercial methods.*

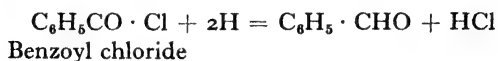(*a*) By heating benzylidene chloride with milk of lime:

$$C_6H_5 \cdot CHCl_2 + Ca(OH)_2 = C_6H_5 \cdot CHO + CaCl_2 + H_2O$$
Benzylidene
chloride
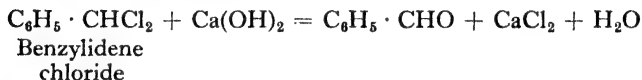
(*b*) By the direct oxidation of toluene with 65 per cent sulphuric acid and manganese dioxide:

$$C_6H_5 \cdot CH_3 + 2O = C_6H_5 \cdot CHO + H_2O$$
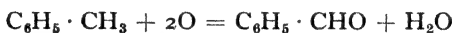
(*c*) By *Étard's Reaction*: oxidation of toluene with chromyl chloride (an intermediate product is first formed):

$$C_6H_5 \cdot CH_3 \longrightarrow C_6H_5 \cdot CH_3 \cdot (CrO_2Cl_2)_2 \longrightarrow C_6H_5 \cdot CHO$$
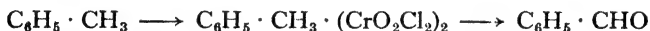
5. By boiling benzyl chloride with aqueous copper or lead nitrate:

$$2C_6H_5 \cdot CH_2Cl + Cu(NO_3)_2 = 2C_6H_5 \cdot CHO + CuCl_2 + 2HNO_2$$
Benzyl chloride
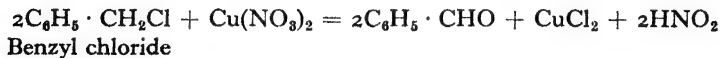
The benzaldehyde formed is extracted with ether, and purified by conversion into the bisulphite compound, from which it is liberated by sulphuric acid.

6. By Grignard's Method (see p. 483).

Properties.—Colourless, highly refractive liquid, m. pt. 26°, b. pt. 179° C. It has an agreeable odour of bitter almonds.

It is sparingly soluble in water but readily soluble in alcohol and ether. It is oxidized on exposure to air to form benzoic acid; the white crust on bottles containing benzaldehyde is benzoic acid. It reacts in the main as an aldehyde, resembling the aliphatic aldehydes.

Reactions.—1. It reduces Tollen's reagent (p. 163).

$$C_6H_5 \cdot CHO + Ag_2O = 2Ag + C_6H_5 \cdot COOH$$

2. It is reduced to benzyl alcohol by sodium amalgam:

$$C_6H_5CHO + 2H = C_6H_5 \cdot CH_2 \cdot OH$$

3. It forms additive compounds with (*a*) sodium bisulphite, (*b*) prussic acid.

$$(a) \quad C_6H_5 - \overset{\overset{\displaystyle H}{|}}{C} = O + H \cdot SO_2 \cdot ONa = C_6H_5 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle SO_2 \cdot ONa.}{|}}{C}} - OH$$

Benzaldehyde sodium
bisulphite or
Benzyl oxysulphonate
of sodium

$$(b) \quad C_6H_5 - \overset{\overset{\displaystyle H}{|}}{C} = O + H \cdot CN = C_6H_5 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}} - OH$$

Benzaldehyde cyanhydrin
or Mandelonitrile
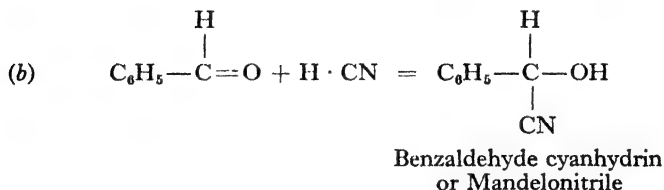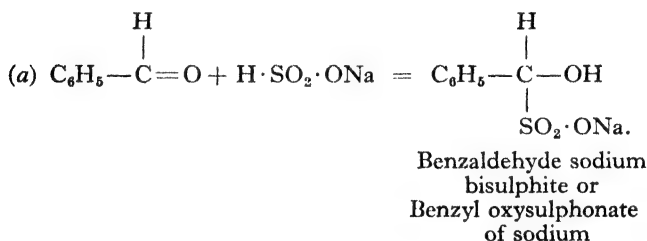
4. It forms a substitution product with ammonia (unlike acetaldehyde, but like formaldehyde):

$$3C_6H_5 \cdot CHO + 2NH_3 = (C_6H_5 \cdot CH)_3N_2 + 3H_2O$$

Hydrobenzamide

$$(cf. \quad 6H \cdot CHO + 4NH_3 = (CH_2)_6N_4 + 6H_2O)$$
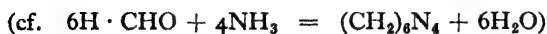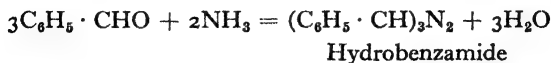
5. It reacts with bases, e.g. aniline, hydroxylamine, phenylhydrazine:

$$C_6H_5—C\!\!\begin{array}{c} H \\ \overline{O + H_2}\cdot N \cdot C_6H_5 \end{array} = C_6H_5—C\!\!\begin{array}{c} H \\ N \cdot C_6H_5 \end{array} + H_2O$$
$$\underset{\text{Aniline}}{} \qquad \underset{\text{Benzylidene aniline}}{}$$

$$C_6H_5—C\!\!\begin{array}{c} H \\ \overline{O + H_2}\cdot NOH \end{array} = C_6H_5—C\!\!\begin{array}{c} H \\ N \cdot OH \end{array} + H_2O$$
$$\underset{\text{Hydroxylamine}}{} \qquad \underset{\alpha\text{-benzaldoxime}}{}$$

$$C_6H_5—C\!\!\begin{array}{c} H \\ \overline{O + H_2}\cdot N \cdot NH \cdot C_6H_5 \end{array} = C_6H_5—C\!\!\begin{array}{c} H \\ N \cdot NH \cdot C_6H_5 \end{array} + H_2O$$
$$\underset{\text{Phenylhydrazine}}{} \quad \underset{\substack{\text{Benzaldehyde phenylhydrazone} \\ \text{(m. pt. } 152° \text{ C.)}}}{}$$
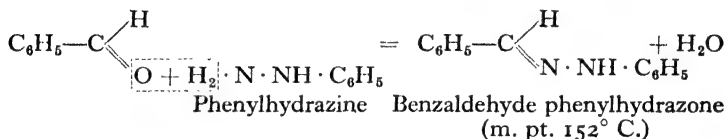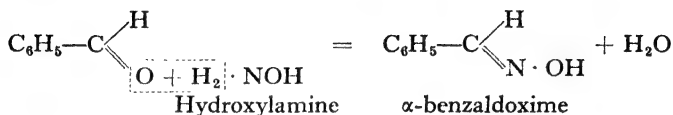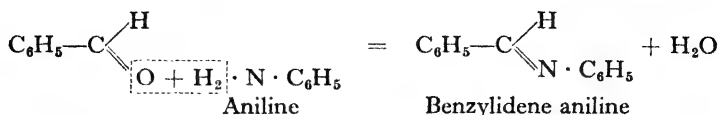
6. It reacts with phosphorus pentachloride to form benzal (benzylidene) chloride:

$$C_6H_5 \cdot CHO + PCl_5 = C_6H_5 \cdot CHCl_2 + POCl_3$$
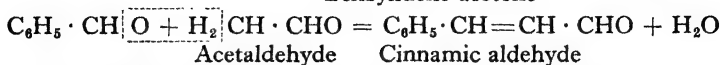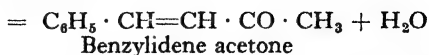$$\underset{\text{Benzal chloride}}{}$$

7. It forms a condensation product known as benzoin when boiled with alcoholic potassium cyanide:

$$C_6H_5 \cdot CHO + HCO \cdot C_6H_5 = C_6H_5 \cdot CH \cdot OH \cdot CO \cdot C_6H_5$$
$$\underset{\text{Benzoin}}{}$$

Notes (*a*) It differs from the aliphatic aldehydes in that no condensation product is formed with acids. With boiling concentrated alkalis it forms condensation products with primary and tertiary amino-compounds, e.g. benzylidene aniline, $C_6H_5CH : N \cdot C_6H_5$.

(*b*) Benzoin is a ketone and a secondary alcohol and contains the group —$CH \cdot OH \cdot CO$— characteristic of the sugars, and hence can reduce Fehling's solution, whereas benzaldehyde does not reduce this solution.

8. *Claisen's Reaction.*—Aromatic aldehydes when condensed with the methylene radicles of many aldehydes and ketones form unsaturated aromatic aldehydes and ketones.

$C_6H_5CH \overline{|O + H_2|} \cdot CH \cdot CO \cdot CH_3$
Acetone

$$= C_6H_5 \cdot CH{=}CH \cdot CO \cdot CH_3 + H_2O$$
Benzylidene acetone

$C_6H_5 \cdot CH \overline{|O + H_2|} CH \cdot CHO = C_6H_5 \cdot CH{=}CH \cdot CHO + H_2O$
Acetaldehyde   Cinnamic aldehyde
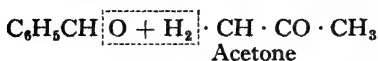
9. *Perkin's Reaction.*—Aromatic aldehydes when condensed with the sodium salts of saturated fatty acids form the sodium salts of unsaturated acids, from which the free acids can be obtained, e.g.:

$C_6H_5 \cdot CH \overline{|O + H_2|} : CH \cdot COONa$
Sodium acetate

$$= C_6H_5 \cdot CH{=}CH \cdot COONa + H_2O$$
Sodium cinnamate
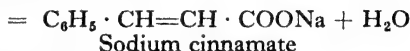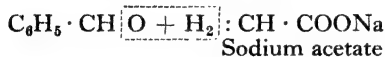
The condensing agent employed is acetic anhydride.

10. *Cannizzaro's Reaction* (p. 418).—This reaction differs from that of the aliphatic aldehydes.

11. Benzaldehyde gives *Schiff's reaction* (p. 167).

Uses.—In the manufacture of triphenylmethane dyes (e.g. malachite green) and of perfumes; and for flavouring, e.g. in almond paste.

C. Ketones

These ketones may be subdivided into two classes:

(*a*) Aromatic-aliphatic ketones, or mixed ketones, e.g. acetophenone (phenyl methyl ketone), $C_6H_5 \cdot CO \cdot CH_3$.

(*b*) Purely aromatic ketones, e.g. benzophenone (diphenyl ketone), $C_6H_5 \cdot CO \cdot C_6H_5$.

Formation.

1. By Friedel and Crafts' reaction from benzene and an acid chloride in the presence of aluminium chloride:

$C_6H_5 \cdot \overline{|H + Cl|} \cdot CO \cdot CH_3 = C_6H_5 \cdot CO \cdot CH_3 + HCl$
Benzene   Acetyl chloride   Acetophenone

$C_6H_5 \cdot \overline{|H + Cl|} \cdot CO \cdot C_6H_5 = C_6H_5 \cdot CO \cdot C_6H_5 + HCl$
Benzene   Benzoyl chloride   Benzophenone
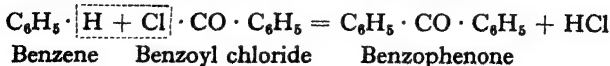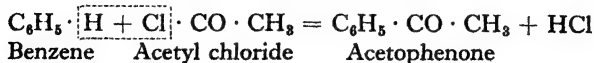
2. By the distillation of the appropriate calcium salt:

$$\left.\begin{array}{l} C_6H_5 \cdot COO \\ CH_3 \cdot COO \end{array}\right\rangle Ca = C_6H_5 \cdot CO \cdot CH_3 + CaCO_3$$

Calcium benzoate   Acetophenone
   and acetate

$$\left.\begin{array}{l} C_6H_5 \cdot COO \\ C_6H_5 \cdot COO \end{array}\right\rangle Ca = C_6H_5 \cdot CO \cdot C_6H_5 + CaCO_3$$

Calcium benzoate   Benzophenone
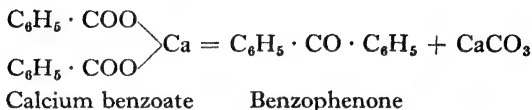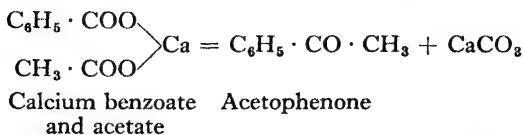
Acetophenone, $C_6H_5COCH_3$, is present in coal tar. It is a white crystalline substance, m. pt. 20° C., b. pt. 202° C., with an agreeable odour. It is sparingly soluble in water but is volatile in steam. It acts both as a ketone and as a benzene derivative.

Reactions.—1. On oxidation (*a*) with ordinary oxidizing agents it is converted into benzoic acid and carbon dioxide.

$$C_6H_5COCH_3 + 2O_2 = C_6H_5COOH + CO_2 + H_2O$$

(*b*) With cold alkaline potassium permanganate, benzoyl formic acid is formed:

$$2C_6H_5COCH_3 + 3O_2 = 2C_6H_5CO \cdot COOH + 2H_2O$$

Phenyl glyoxylic
acid (Benzoyl
formic acid)
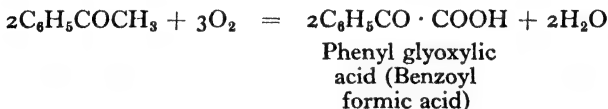
2. On reduction it is converted into a secondary alcohol:

$$C_6H_5COCH_3 + 2H = C_6H_5 \cdot CHOH \cdot CH_3$$

Phenyl methyl carbinol
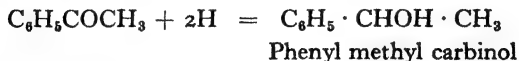
3. With halogens, substitution takes place in the side-chain:

$$C_6H_5COCH_3 + Br_2 = C_6H_5CO \cdot CH_2Br + HBr$$

Phenacyl bromide
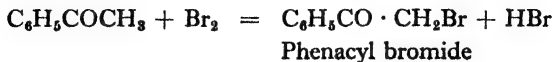
4. With prussic acid, it forms an additive product (cyanhydrin) which is hydrolysed to a hydroxy acid:
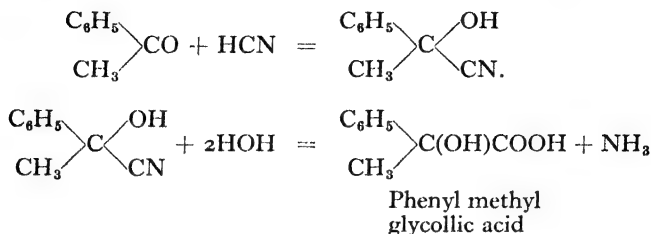
$$\begin{array}{l} C_6H_5 \\ \qquad \diagdown CO + HCN \\ CH_3 \diagup \end{array} = \begin{array}{l} C_6H_5 \\ \qquad \diagdown C \diagup ^{OH}_{CN}. \\ CH_3 \diagup \end{array}$$

$$\begin{array}{l} C_6H_5 \\ \qquad \diagdown C \diagup ^{OH}_{CN} + 2HOH \\ CH_3 \diagup \end{array} = \begin{array}{l} C_6H_5 \\ \qquad \diagdown C(OH)COOH + NH_3 \\ CH_3 \diagup \end{array}$$

<div align="center">Phenyl methyl
glycollic acid</div>

5. With hydroxylamine it forms an oxime (m. pt. 59° C.):

$$\begin{array}{l} C_6H_5 \\ \qquad \diagdown C = \boxed{O + H_2}NOH \\ CH_3 \diagup \end{array} = \begin{array}{l} C_6H_5 \\ \qquad \diagdown C = N \cdot OH + H_2O \\ CH_3 \diagup \end{array}$$

6. With phenylhydrazine it forms a phenyl-hydrazone (m. pt. 105° C.):

$$\begin{array}{l} C_6H_5 \\ \qquad \diagdown C = \boxed{O + H_2}N \cdot NHC_6H_5 \\ CH_3 \diagup \end{array} = \begin{array}{l} C_6H_5 \\ \qquad \diagdown C = N \cdot NHC_6H_5 + H_2O \\ CH_3 \diagup \end{array}$$
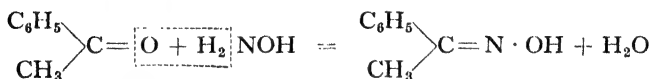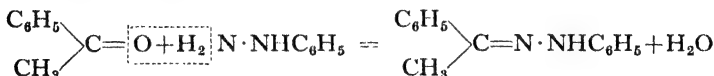
Acetophenone is sometimes used in medicine as a soporific under the name of *hypnone*.

Benzophenone, $C_6H_5COC_6H_5$, is a white crystalline substance, m. pt. 48° C., b. pt. 305° C. It is dimorphous, the stable form when boiled or distilled being converted into the unstable modification (m. pt. 26° C.). On standing the unstable form reverts to the stable form. Benzophenone is insoluble in water but soluble in alcohol and ether.

Reactions.—1. On oxidation with chromic acid it is converted into benzoic acid; one of the phenyl groups being destroyed in the reaction:

$$C_6H_5 \cdot CO \cdot C_6H_5 + 15O = C_6H_5COOH + 6CO_2 + 2H_2O$$

2. On reduction (*a*) with sodium amalgam, a secondary alcohol is formed:

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!CO + 2H = \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!CH \cdot OH$$

Benzhydrol
(Diphenyl carbinol)
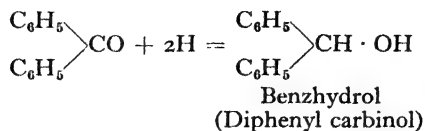
(*b*) with zinc dust or with hydriodic acid and red phosphorus diphenylmethane (m. pt. 26° C.) is formed:
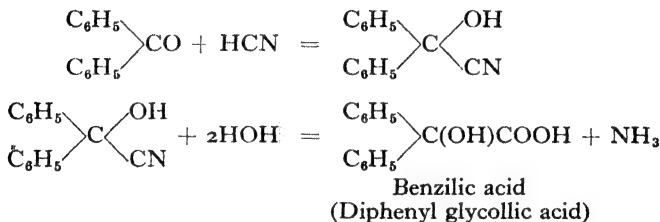
$$C_6H_5 \cdot CO \cdot C_6H_5 + 2H_2 = C_6H_5 \cdot CH_2 \cdot C_6H_5 + H_2O$$

Diphenylmethane

3. With prussic acid it forms a cyanhydrin which can be hydrolysed to benzilic acid:

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!CO + HCN = \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} OH \\ CN \end{matrix}$$

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} OH \\ CN \end{matrix} + 2HOH = \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!C(OH)COOH + NH_3$$

Benzilic acid
(Diphenyl glycollic acid)

4. With hydroxylamine it forms an oxime (m. pt. 141° C.):

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!C = \boxed{O + H_2}\,N \cdot OH = \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!C = N \cdot OH + H_2O$$

5. With phenylhydrazine it forms a phenylhydrazone (m. pt. 137° C.):

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!C = \boxed{O + H_2}\,N \cdot NHC_6H_5 = \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!C = N \cdot NHC_6H_5 + H_2O$$
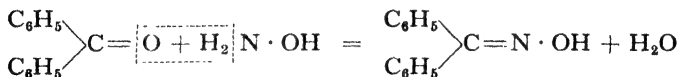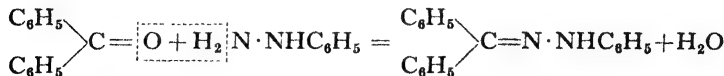
The aromatic ketones, however, do not form bisulphite compounds. Moreover, as in most aromatic compounds, the benzene nucleus can be nitrated, sulphated, &c. (contrast the aliphatic homologues).

QUINONES

The aromatic series also differs from the aliphatic in forming special unsaturated double ketones known as **quinones.** They have formulæ of the type $C_6H_4O_2$, and are of two types, the ortho-quinones and the para-quinones. They are characterized by two carbonyl $=CO$ groups directly linked to the benzene nucleus.

Ortho-quinone is formed on the oxidation of catechol by silver oxide:

Catechol   Benzene
                        o-quinone

Benzene orthoquinone is obtained as bright-red crystals. The structural formula represented in the equation shows that this quinone is a ketone with the $=CO$ groups in the ortho position. This is verified by its " ketonic " reactions.

Quinone is formed by the oxidation of (a) quinol with ferric chloride or (b) aniline with chromic acid:

Quinol   Quinone

This is the ordinary quinone of commerce. It is obtained as yellow needles, m. pt. 115° C. It sublimes when heated and is volatile in steam. The structural formula differs from

that of the ortho compound, the two ═CO groups being
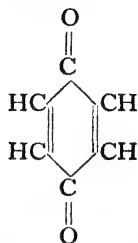in the para-position.

The structural formulæ of the quinones indicated below
show that the arrangement of the carbon valencies cannot
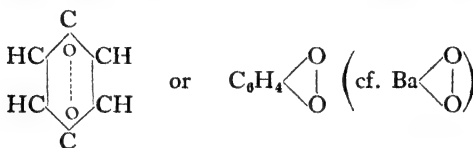be the same as in benzene:
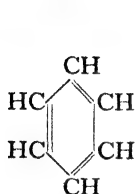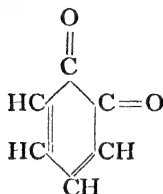
Benzene   *o*-quinone   Quinone

It has also been suggested that the two oxygen atoms are
directly linked together, so that the quinones are peroxides:

This formula cannot be accepted, since ordinary quinone
in its various reactions does not act as a peroxide.

The double ketonic structure of quinone is supported by
the formation of two oximes with hydroxylamine, and its
unsaturated ethylenic groups by the formation of quinone
tetrabromide on treatment with bromine:

Quinone   Quinone   Quinone
monoxime   dioxime   tetrabromide
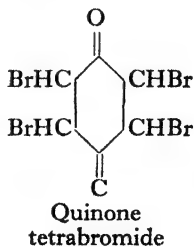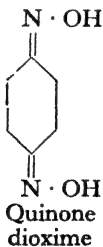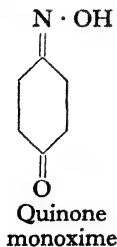
On reduction with sulphurous acid, quinone is converted into hydroquinone (quinol):
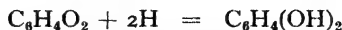
$$C_6H_4O_2 + 2H = C_6H_4(OH)_2$$

Hydroquinone is obtained as colourless crystals, m. pt. 169° C., which are readily soluble in water.

QUESTIONS

1 Indicate a series of reactions whereby benzaldehyde may be obtained from benzene. Compare its reactions with those of acetaldehyde. Describe carefully how you would prepare from benzaldehyde a well-crystallized specimen of benzoic acid.

(*Oxford Higher School Cert.*)

2. A compound was found to contain carbon, hydrogen and oxygen only, and on analysis gave carbon 80·0 per cent and hydrogen 6·6 per cent. Its vapour density was 60 (H = 1).

On oxidation it gave an acid which when heated with lime gave benzene.

Deduce structural formulæ for the compound and state how you would distinguish between them.

3. Compare and contrast the preparation and chemical properties of benzoic acid and acetic acid.

4. Describe the preparation of benzoic acid either from benzaldehyde or from benzyl chloride.

Mention the chief properties of benzoic acid and state briefly how you would attempt to obtain from it (*a*) benzene, (*b*) ethyl benzoate, (*c*) benzoyl chloride.   (*Cambridge Higher School Cert.*)

5. Starting with benzene, how may (*a*) toluene, (*b*) salicylic acid, (*c*) benzoic acid, (*d*) phenol be prepared? How may benzene be obtained from each of these substances?

6. Outline the preparation from toluene of (*a*) benzaldehyde, (*b*) benzoic acid.

By what tests would you distinguish between benzoic acid and phenol?

7. How is benzaldehyde prepared commercially? Give one method for its preparation and indicate its reactions with (*a*) alcoholic potassium cyanide, (*b*) hydroxylamine, (*c*) hydrocyanic acid and (*d*) hot concentrated aqueous alkali.   (*B.Sc. General, London.*)

CHAPTER XVIII

Amino-derivatives of Benzene

The amino-derivatives of the paraffins are made mainly by treating the halogen derivatives with ammonia, whereas those of the benzene hydrocarbons are made mainly by treating nitro-compounds with nascent hydrogen.

They may be regarded:

1. As benzene hydrocarbons in which a hydrogen atom of the nucleus is replaced by the amino-group —NH_2, i.e. as substituted derivatives of benzene. The hydrogen in the side chain may, however, also be replaced, as in benzylamine.

| Benzene | Aniline | Toluene | p-toluidine | Benzylamine |
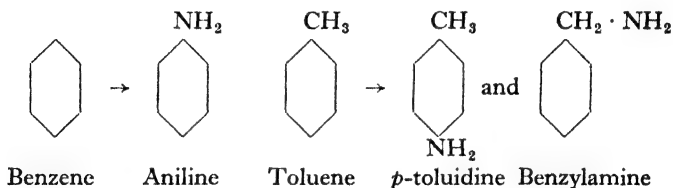
2. As ammonia in which a hydrogen atom is replaced by the phenyl-group —C_6H_5 or other aromatic radicle, i.e. as substituted ammonias. The most important amino-derivative of benzene, aniline, will be discussed as an illustration.
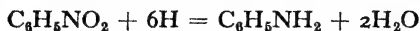
Aniline, Amino-benzene, Phenylamine, $C_6H_5NH_2$.

The name aniline is derived from *alnil*, the Arabic name for indigo, from which it was first obtained in 1826 by Unverdorben, by distillation.
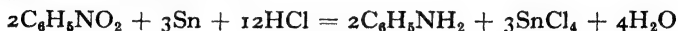
Aniline is found in coal tar and in bone oil.

Formation.

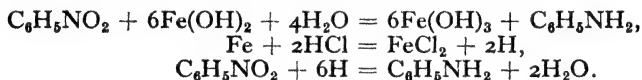1. By reducing nitrobenzene with nascent hydrogen:

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O$$

The nascent hydrogen is obtained in the laboratory by the action of tin on hydrochloric acid. The reaction is represented as follows:

$$2C_6H_5NO_2 + 3Sn + 12HCl = 2C_6H_5NH_2 + 3SnCl_4 + 4H_2O$$

Commercially the reduction is brought about by ferrous chloride, iron and water. The ferrous chloride is formed by the action of a regulated small quantity of hydrochloric acid on iron filings. The ferrous chloride is hydrolysed in the presence of iron and water to ferrous hydroxide and hydrochloric acid:

$$FeCl_2 + 2HOH \rightleftharpoons Fe(OH)_2 + 2HCl$$
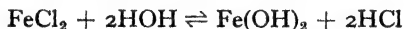
The hydroxide at once reduces some of the nitrobenzene to aniline, while the iron reacts with the liberated acid to regenerate ferrous chloride and to produce nascent hydrogen, which reduces more of the nitrobenzene as follows:

$$C_6H_5NO_2 + 6Fe(OH)_2 + 4H_2O = 6Fe(OH)_3 + C_6H_5NH_2,$$
$$Fe + 2HCl = FeCl_2 + 2H,$$
$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O.$$

Thus a small amount of ferrous chloride only is necessary to bring about the reduction.

This is a general method for the preparation of primary aromatic amino-compounds (amines).

Experiment.—To prepare aniline and to examine its properties: Place in a 1 to 2 litre round-bottomed flask 40 c.c. of nitrobenzene and 80 gm. of granulated tin. Fit the flask with a cork and an upright air condenser about 2 ft. long. Warm the mixture on the water bath for 5 min. Remove the flask and add concentrated hydrochloric acid (sp. gr. 1·16), about 10 c.c. at a time, until about 200 c.c. have been added. Shake repeatedly. The addition of the acid should take at least half an hour. The liquid becomes hot, and if the action becomes too violent the flask should be cooled under

the tap. The flask is then replaced on the water bath without the condenser and heated for an hour or until all the oily drops of nitrobenzene have disappeared. It must not be allowed to cool, as the mass solidifies.

Whilst the solution is hot add 100 c.c. of water and 200 c.c. of a 70 per cent solution of caustic soda slowly, so that the stannic oxide which is first precipitated redissolves. The alkali must be added in excess, and the solution cooled if necessary. Aniline now separates out as a dark-coloured oil and is then subjected to **Steam Distillation.**

The apparatus is set up as in fig. 40 (p. 448). The flask F contains the aniline, and is heated gently on a sand bath, and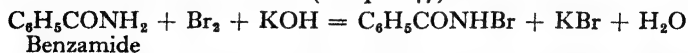 the tube from the steam boiler B is bent as shown, so that when steam is passed through the hot solution the contents will not splash over into the condenser. The aniline should be heated to boiling-point before the steam is admitted. Aniline and water collect in the receiver R. The operation is at an end when a clear distillate instead of a milky one is seen. The aniline is extracted by saturating the distillate with salt in a separating funnel and treating the solution with ether. The salt solution is run off and the ethereal solution, which contains the aniline, is dried over solid potash and decanted into a dry flask and the ether is then distilled off from a water bath. The aniline is finally purified by distillation.

2. By heating amino-acids alone or with soda-lime:

$$C_6H_4{<}^{NH_2}_{COOH} = C_6H_5NH_2 + CO_2$$

Amino-benzoic acid   Aniline
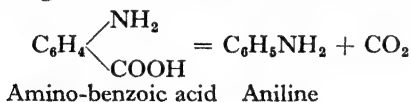
3. *Hofmann's Method.*—By treating benzamide with bromine and caustic alkali (see p. 147):

$C_6H_5CONH_2 + Br_2 + KOH = C_6H_5CONHBr + KBr + H_2O$
Benzamide

$C_6H_5CONHBr + 3KOH = C_6H_5NH_2 + KBr + K_2CO_3 + H_2O$
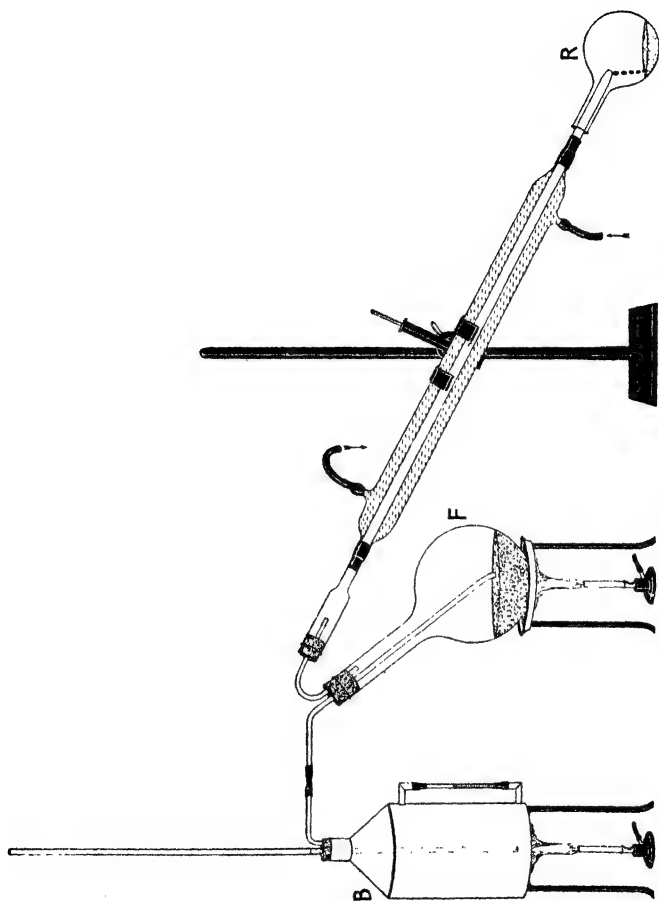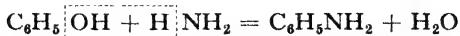Aniline

This is a general method for the preparation of primary amines.

Fig. 40.—Preparation of Aniline:—Steam Distillation

4. By heating phenol with ammonia in the presence of zinc or calcium chloride:

$$C_6H_5\overline{|OH + H|}NH_2 = C_6H_5NH_2 + H_2O$$

Properties.—Aniline is a colourless, highly refractive liquid with an oily appearance and a characteristic odour, b. pt. 183° C., m. pt. −6°, sp. gr. 1·0265 at 15° C. It turns yellow when exposed to air and light, eventually becoming almost black.

Reactions.—1. Shake up a few drops of aniline with water and add litmus solution: the liquid is sparingly soluble and neutral. Being heavier than water, it sinks to the bottom.

2. Aniline forms well-defined crystalline salts with acids. Its basic properties are shown by taking a few drops of aniline in a test tube and adding drop by drop a 50 per cent solution of hydrochloric acid until the aniline dissolves; aniline hydrochloride, $C_6H_5NH_2 \cdot HCl$, is formed. To this salt add water; it will be observed that a clear solution remains. Aniline hydrochloride is known commercially as *aniline salt*, and is used in the production of aniline black on fabrics by oxidation.

Repeat with sulphuric acid; the product is aniline sulphate, $(C_6H_5NH_2)_2 \cdot H_2SO_4$. This salt is sparingly soluble in water. The aniline can be liberated from these salts by the addition of slight excess of alkali. Hence aniline can be regarded as a mon-acid base forming salts like ammonia, or as a substituted ammonia. Since aniline is a very weak base, its salts are acid in solution.

3. *Carbylamine Reaction*.—Take one drop of aniline, a few drops of chloroform and 2 c.c. of alcoholic potash in a test tube and warm (in a fume cupboard). Note the intolerable smell of phenyl carbylamine:

$$C_6H_5NH_2 + CHCl_3 + 3KOH = C_6H_5N \overset{\cdot\cdot}{\cdot} C + 3KCl + 3H_2O$$
<div align="center">Phenyl
carbylamine</div>
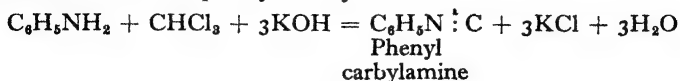
(Characteristic of primary amines, both aliphatic and aromatic).

4. Solubility.—Shake up a few drops of aniline with alcohol, ether and benzene, and note that it is soluble in all these solvents.

5. Aniline forms diazo-compounds (p. 469). Dissolve a few drops of aniline in 4 c.c. of dilute hydrochloric acid and add about 1 c.c. of sodium nitrite solution; a diazo-compound is formed:

Aniline
hydrochloride

Benzene (phenyl)
diazonium chloride
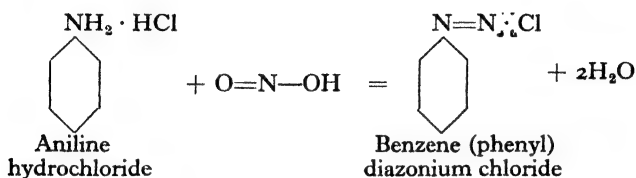
This diazo-salt is derived from a strong base known as phenyl diazonium hydroxide, or diazobenzene hydrate, $C_6H_5 \cdot N=N \cdot OH$.

Diazotization is the conversion of amino-compounds into diazo-compounds.

(a) Pour half the above solution into 0·5 gm. of phenol dissolved in 2 c.c. of caustic soda solution: an orange-red solution of sodium hydroxy-azobenzene is formed:

Benzene
diazonium
chloride

Phenol

$$= \bigotimes N=N \bigotimes ONa + 2H_2O + NaCl$$

Sodium hydroxy-azobenzene
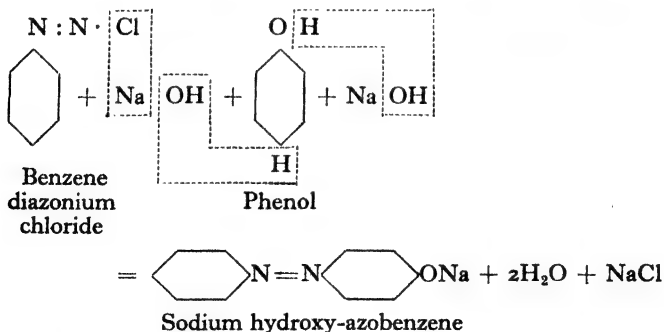
This is used as a test for a primary aromatic amine with the —NH_2 group in the nucleus. An azo-dye is produced, coloured yellow, red-brown or orange.

(b) Warm the other half of the solution: effervescence occurs. Nitrogen is evolved and a smell of carbolic acid observed:

$$C_6H_5N{=}NCl + HOH = C_6H_5OH + N_2 + HCl$$

By substituting nitric acid or sulphuric acid for hydrochloric acid and subsequently treating the aniline nitrate and aniline sulphate with nitrous acid, phenyl diazonium nitrate, $C_6H_5 \cdot N = N \cdot NO_3$, and phenyl diazonium sulphate, $(C_6H_5N{=}N)_2SO_4$, are formed respectively.

6. Add one drop of aniline to a solution of sodium hypochlorite or bleaching powder: an intense violet coloration is produced:

$$C_6H_5NH_2 \rightarrow C_6H_5NHCl \rightarrow C_6H_4ClNH_2$$

7. Add one drop of aniline to 5 drops of concentrated sulphuric acid placed in a basin, stir and then add 5 drops of potassium dichromate solution: an intense blue colour (red at first) is produced.

· The oxidation of aniline affords an excellent example of the variety of products obtained according to the oxidizing agent employed:

Oxidizing Agent	Products
(a) Chromic acid.	(a) Quinone.
(b) Manganese dioxide and sulphuric acid.	(b) Ammonia and a little quinone: $$C_6H_5NH_2 + O_3 = NH_3 + C_6H_4O_2.$$
(c) Neutral $KMnO_4$.	(c) Nitrobenzene and azobenzene: $$C_6H_5NH_2 + 3O = C_6H_5NO_2 + H_2O,$$ $$2C_6H_5NH_2 + O_2 = C_6H_5N{=}NC_6H_5 + 2H_2O.$$
(d) Acid $KMnO_4$.	(d) Aniline black.
(e) Alkaline $KMnO_4$.	(e) Ammonia and azobenzene.
(f) Bleaching powder.	(f) Nitrobenzene.
(g) Hypochlorous acid.	(g) p-amino-phenol: $$C_6H_5NH_2 + O = C_6H_4(OH)NH_2.$$
(h) Permonosulphuric acid. (Caro's acid.)	(h) Nitrosobenzene: $$C_6H_5NH_2 + 2H_2SO_5$$ $$= C_6H_5 \cdot NO + 2H_2SO_4 + H_2O.$$

8. It forms substituted products with the halogens. Dissolve a few drops of aniline in hydrochloric acid. Add bromine water drop by drop until a faint brown colour persists on shaking. A colourless precipitate of tribromaniline is obtained, which may be recrystallized from glacial acetic acid.

s-tribromaniline
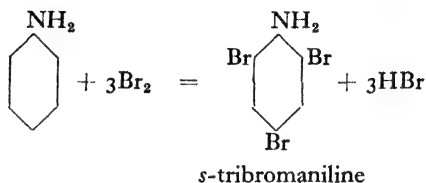
9. Mix together 0·2 gm. of aniline and 0·2 gm. of phenyl isocyanate. Heat is generated and the mixture solidifies, forming diphenyl urea, which may be extracted and recrystallized from alcohol (colourless needles, m. pt. 238° C.):

$$C_6H_5NH_2 + C_6H_5N{=}CO = C_6H_5NH \cdot CO \cdot NHC_6H_5$$
Diphenyl urea
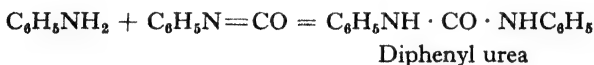
10. It forms secondary and tertiary amines. It reacts with methyl iodide and other alkyl iodides to form secondary, tertiary, and quaternary compounds, like the aliphatic primary amines, e.g.

$$C_6H_5NH_2 + CH_3I = C_6H_5NH(CH_3) \cdot HI,$$
$$C_6H_5NH(CH_3) + CH_3I = C_6H_5N(CH_3)_2 \cdot HI,$$
$$C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I.$$
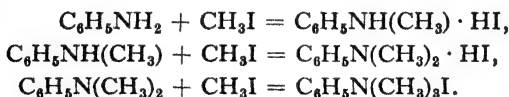
It should be noted, however, that purely aromatic quaternary compounds have not been prepared.

11. It condenses with aldehydes with the elimination of a molecule of water:

$$C_6H_5NH_2 + C_6H_5CHO = C_6H_5 \cdot CH{=}N \cdot C_6H_5 + H_2O$$

Structurally:

N H_2 O HC

Aniline Benzaldehyde   Benzylidene aniline
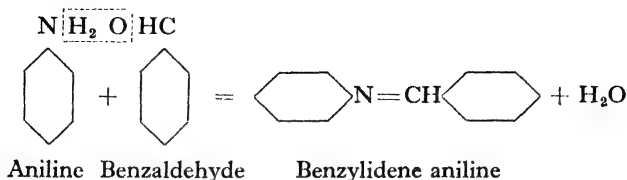
Uses.—Aniline is used in the preparation of stains, e.g. safranine, rosaniline blue; of dyestuffs and synthetic indigo; of substances for making drugs; and as an accelerator in the vulcanization of rubber.

General Properties of the Amino-Compounds.

These are similar to those described under the reactions of aniline. The amino-compounds are usually colourless liquids and solids, sparingly soluble in water, volatile in steam, and with a faint characteristic smell. They are bases, forming well-defined salts with acids and double salts with platinic chloride. Aniline platinichloride is yellow and sparingly soluble in water:

$$2[C_6H_5NH_2 \cdot HCl] + PtCl_4 = (C_6H_5NH_2)_2 \cdot H_2PtCl_6$$

The hydrochlorides and nitrates are usually very soluble, but the sulphates are sparingly soluble in water.

The bases are neutral, but the salts are acid to litmus. The aromatic amino-compounds are weaker bases than the aliphatic amines, and their neutrality results from the fact, that the benzene radicle —C_6H_5 possesses a negative character, whereas the alkyl radicles are positive.

The amino-compounds form secondary and tertiary bases,

the hydrogen atoms of the amino group being replaced by radicles, as follows:

Primary	Secondary	Tertiary	

$$
\begin{array}{ccc}
& C_6H_5 & \\
& \diagup & \\
N & \!\!—H & \\
& \diagdown & \\
& H &
\end{array}
\qquad
\begin{array}{ccc}
& C_6H_5 & \\
& \diagup & \\
N & \!\!—C_6H_5 & \\
& \diagdown & \\
& H &
\end{array}
\qquad
\begin{array}{ccc}
& C_6H_5 & \\
& \diagup & \\
N & \!\!—C_6H_5 & \\
& \diagdown & \\
& C_6H_5 &
\end{array}
\qquad
\text{Aromatic amines}
$$

Aniline or   Diphenylamine   Triphenylamine
Phenylamine   (very weak base)   (neutral)
(weak base)
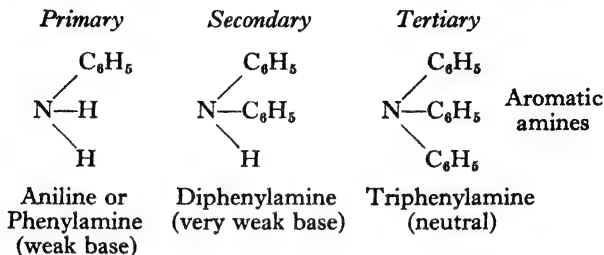
The substitution of aromatic radicles for the hydrogen atoms leads to a progressive decrease in the basic character of the compound. Triphenylamine forms no salts.

$$
\begin{array}{ccc}
& C_6H_5 & \\
& \diagup & \\
N & \!\!—H & \\
& \diagdown & \\
& H &
\end{array}
\qquad
\begin{array}{ccc}
& C_6H_5 & \\
& \diagup & \\
N & \!\!—C_2H_5 & \\
& \diagdown & \\
& H &
\end{array}
\qquad
\begin{array}{ccc}
& C_6H_5 & \\
& \diagup & \\
N & \!\!—C_2H_5 & \\
& \diagdown & \\
& C_2H_5 &
\end{array}
\qquad
\text{Mixed amines}
$$

Aniline   Ethylaniline   Diethylaniline
(weak base)   (slightly stronger   (much stronger
           base)   base)
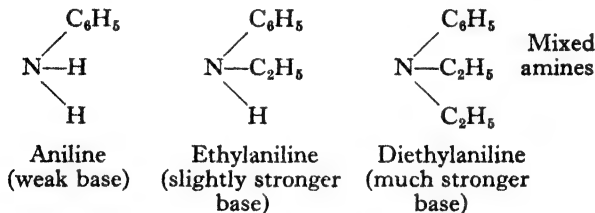
The substitution of alkyl radicles for the hydrogen atoms leads to a progressive increase in the basic character of the compound. The quaternary bases are strongly alkaline, e.g. $C_6H_5N(C_2H_5)_3OH$.

Distinctions between the Amino-Compounds.

The three classes of amino-compounds may be distinguished by the employment of the same reagents as are used to distinguish aliphatic amines, although similar results are not obtained in each case.

The following is a summary of the products formed:

Reagent	Primary	Secondary	Tertiary
1. Nitrous acid	(a) Diazo-com-pound (b) Phenol and nitrogen	Nitrosamine	Nitroso-compound
2. Alkyl iodides	Negative	Negative	Quaternary ammonium compound
3. Acetyl chloride or acetic anhydride	Acetyl deri-vative (e.g. Acetanilide)	Acetyl deri-vative (e.g. Methyl acet-anilide	No acetyl derivative
4. Carbyl-amine test: chloroform and alco-holic potash	Positive, forms isocyanide	Negative	Negative
5. Carbon disulphide	Hydrogen sul-phide evolved	Negative	Negative

Primary amines on treatment with nitrous acid below 10° C. give **Diazo-compounds** (pp. 450, 469)):

$$C_6H_5N|H_2 + O|=N—OH = C_6H_5N=N \cdot OH + H_2O$$
Diazobenzene hydrate
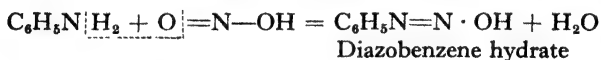
If this compound is warmed, nitrogen is evolved and phenol is formed:

$$C_6H_5N=N \cdot OH = C_6H_5OH + N_2$$
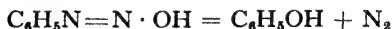
Secondary amines with nitrous acid form insoluble yellow substances known as **Nitrosamines,** e.g. diphenyl-amine yields diphenylnitrosamine:

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \!\!\!>\!\! N|H + HO| \cdot N=O = \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \!\!\!>\!\! N \cdot N=O + HOH$$
Diphenylamine   Diphenylnitrosamine

Structurally:

$$\text{C}_6\text{H}_5\text{—N}\text{—C}_6\text{H}_5 = \text{C}_6\text{H}_5\text{—N}\text{—C}_6\text{H}_5 + \text{HOH}$$
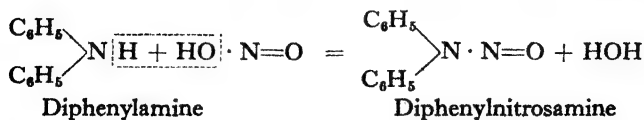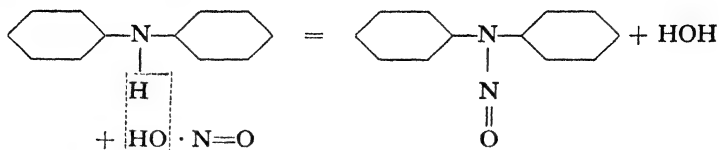
Experiment.—Dissolve a few drops of diphenylamine in a slight excess of dilute hydrochloric acid and add a few drops of sodium nitrite solution. A precipitate of diphenylnitrosamine is formed, which may be extracted with ether. Repeat using methylaniline.

Liebermann's nitroso-reaction is employed as a further test; it consists in dissolving a few crystals of phenol in about 2 c.c. of concentrated sulphuric acid and adding one drop of the nitroso-compound to this solution. On adding excess of alkali and warming a blue compound is formed, which changes to red on dilution with water.

This reaction affords a test for secondary amines as well as for phenols.

Tertiary amines with nitrous acid form **Nitrosocompounds,** the para-hydrogen of the nucleus being replaced, e.g.

Dimethylaniline   Nitroso-dimethylaniline
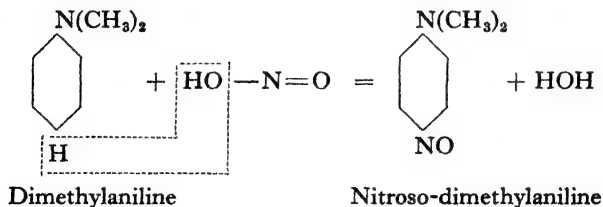
A purely aromatic tertiary amine, such as triphenylamine, is not acted on by nitrous acid.

Primary and secondary amines react with acetyl

chloride or acetic anhydride to form acetyl derivatives; such compounds are not formed with tertiary amines.

$$C_6H_5NH_2 + CH_3COCl = C_6H_5NH \cdot CO \cdot CH_3 + HCl$$

Aniline   Acetyl chloride   Acetanilide
(b. pt. 304° C.)

$$2C_6H_5NH(CH_3) + \begin{array}{c} CH_3CO \\ \diagdown \\ CH_3CO \diagup \end{array} O = 2C_6H_5N(CH_3) \cdot CO \cdot CH_3 + H_2O$$

Methylaniline   Acetic   Methyl acetanilide
                  anhydride   (b. pt. 237° C.)
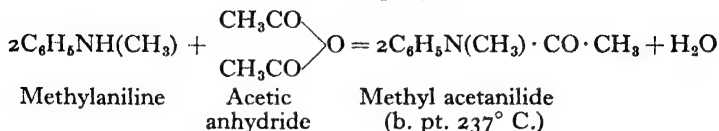
This reaction serves as a means of separating amines. The tertiary amine, e.g. dimethylaniline, $C_6H_5N(CH_3)_2$, is the most volatile, boiling at 193° C., so on distillation it separates first.

Experiment.—Take three test tubes containing 10 drops each of aniline, methylaniline and dimethylaniline respectively, and add 10 drops of acetic anhydride to each test tube. Warm for a minute over a small flame and pour into separate beakers of water.

Aniline and methylaniline give solid crystalline precipitates. Dimethylaniline is unchanged and remains a liquid.

Primary amines (*a*) give the carbylamine reaction (p. 449); (*b*) when mixed with carbon disulphide (CS_2) diluted with alcohol and boiled in a flask fitted with a reflux condenser, they give off hydrogen sulphide, which is detected by means of lead acetate paper, and on cooling a colourless crystalline substance known as thiocarbanilide separates out:

$$\begin{array}{c} C_6H_5NH \cdot \text{H} \\ \quad\quad\quad\; + S \; CS = \\ C_6H_5NH \cdot \text{H} \end{array} \begin{array}{c} C_6H_5NH \\ \diagdown \\ C_6H_5NH \diagup \end{array} C{=}S + H_2S$$

Thiocarbanilide
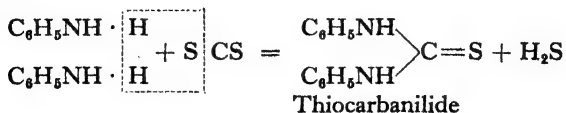
Neither of these reactions is given by secondary and tertiary amines.

Tertiary amines form quaternary ammonium iodides with alkyl iodides. Dimethylaniline when warmed with methyl iodide forms a crystalline substance known as trimethylphenyl ammonium iodide:

$$\underset{\text{}}{\overset{N(CH_3)_2}{\bigcirc}} \quad + CH_3I \quad = \quad \overset{N(CH_3)_3I}{\bigcirc}$$
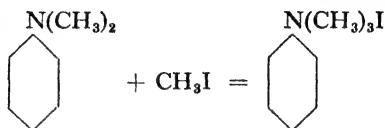
This type of compound is not formed with primary and secondary amines.

DERIVATIVES OF ANILINE

Halogen Derivatives. Chlorine and bromine water react with aniline to precipitate trichlor- and tribromaniline respectively, e.g.

$$\underset{\text{Aniline}}{\overset{NH_2}{\bigcirc}} + 3Br_2 \quad = \quad \underset{2:4:6 \text{ tribromaniline}}{\overset{NH_2}{\underset{Br}{\overset{Br}{\bigcirc}}Br}} + 3HBr$$
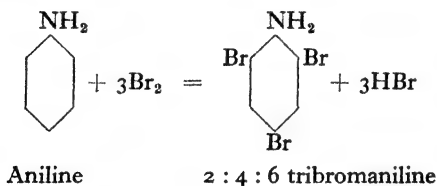
The formation of symmetrical tribromaniline by bromination of aniline, and the ease with which this substitution takes place, are due to the fact that the bromine first of all displaces one of the hydrogen atoms of the —NH_2 group to form phenylbromamide, C_6H_5NHBr, which is very unstable and undergoes intramolecular change, the —NH_2 group directing the bromine atom to the ortho- or para-position (see p. 464); this continues until the ortho- and para-positions are satisfied.

Chlorine behaves in a similar way.

Acetanilide, Phenylacetamide, $C_6H_5NH \cdot COCH_3$, is formed when aniline is acetylated, that is, treated with acetyl chloride, acetic anhydride or glacial acetic acid. On the large scale glacial acetic acid is used:

NH$_2$ NH $\cdot$ CO $\cdot$ CH$_3$

$$\bigcirc + CH_3 \cdot CO \cdot Cl = \bigcirc + HCl$$

Aniline   Acetanilide
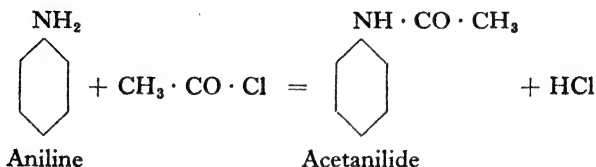
It is a white crystalline solid, m. pt. 114° C., b. pt. 304° C., sparingly soluble in cold water, but readily soluble in alcohol. It is extensively used in medicine as a febrifuge (i.e. to mitigate fever) under the name of *antifebrin*. It is hydrolysed by boiling alkalis or acids:

$$C_6H_5 \cdot NH \cdot |CO \cdot CH_3 = C_6H_5NH_2 + CH_3COOH$$
$$+ H|OH$$
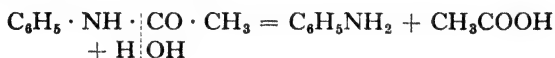
Experiment.—To prepare acetanilide (see also p. 571).

Mix together about 20 c.c. of aniline and 30 c.c. of glacial acetic acid in a 250 c.c. round-bottomed flask fitted with a reflux air condenser about 2 ft. long, to condense the acetic acid which vaporizes. Boil gently for over an hour and pour the hot contents into a litre of water contained in a beaker. The acetanilide is precipitated as a crystalline mass. Filter, wash and recrystallize from hot water; filter again and dry. Then (*a*) take the melting-point of the dry solid; (*b*) to about 0·5 gm. in a test tube add 3 c.c. of concentrated hydrochloric acid and heat on the water bath for a few minutes. On dilution with water a clear solution is obtained; the acetanilide has been hydrolysed to aniline and acetic acid. Then add excess of caustic soda and note that oily globules of aniline are set free, which may be extracted with ether as already described (p. 447).

Phenacetin or ***p*-ethoxy-acetanilide** is a well-known

derivative of acetanilide formed by boiling acetic acid with *p*-ethoxy-aniline (*p*-phenetidine):

$$NH[H + HO]OC \cdot CH_3 \qquad\qquad NH \cdot OC \cdot CH_3$$

Acetic acid   = $+ H_2O$

OC_2H_5 OC_2H_5
p-phenetidine   Phenacetin
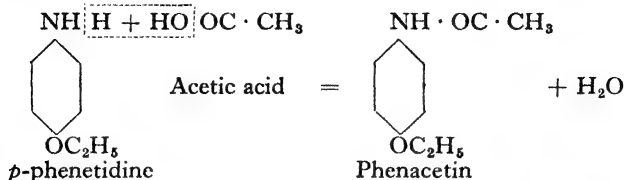
It is a white crystalline solid, m. pt. 135°, sparingly soluble in water, and is used in medicine to alleviate pain and to reduce temperature.

Nitranilines.—Aniline reacts vigorously with concentrated nitric acid; as the base is so sensitive to the action of oxidizing agents it is necessary to " protect " the amino group, either by using the acetyl derivative or by nitrating in the presence of excess of concentrated sulphuric acid, otherwise nitrobenzene is formed. On nitration the para-compound is generally formed with a little of the ortho-compound:

NH_2 NH_2 NH_2

→   and NO_2

$[H]$ NO_2
$+ [HO] \cdot NO_2$

                 p-nitraniline   *o*-nitraniline
               (m. pt. 147° C.)   (m. pt. 71° C.)
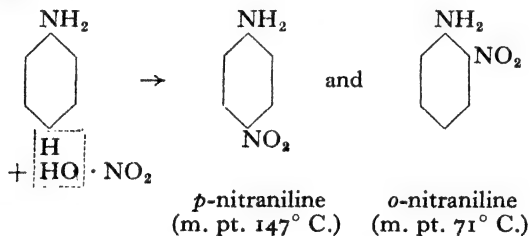
The meta-compound is made commercially by the reduction of one of the nitro-groups of *m*-dinitrobenzene with sodium or ammonium polysulphide:

NO_2 NO_2

$+ Na_2S_2 + H_2O$ $+ Na_2S_2O_3$

NO_2 = NH_2
m-dinitrobenzene   *m*-nitraniline
                       (m. pt. 114° C.)
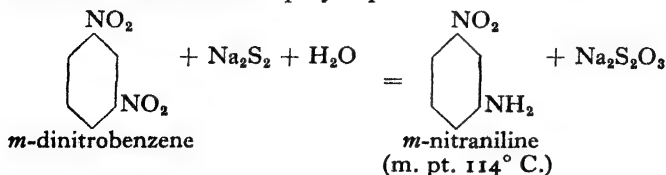
Ortho- and para-nitranilines can be obtained by nitrating acetanilide directly with concentrated nitric acid, since the acetyl group present protects the amino-group from oxidation. The ortho- and para- nitro-acetanilides thus produced are easily converted into the corresponding nitranilines on hydrolysis:

NH · COCH₃   + HONO₂ =   NH · COCH₃ / NO₂   + HOH

Acetanilide   o-nitro-acetanilide

=   NH₂ / NO₂   + CH₃COOH
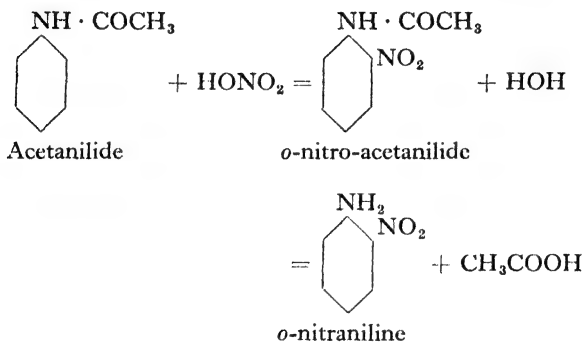
o-nitraniline

The nitranilines crystallize as yellow needles, sparingly soluble in water, but readily soluble in alcohol.

The ortho- and para-compounds, but not the meta-compound, undergo hydrolysis when boiled with alkalis, yielding *nitrophenols*:

NH₂ ... NO₂   + HOH   =   OH ... NO₂   + NH₃

p-nitrophenol
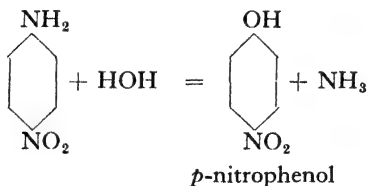
Sulphanilic Acid, *p*-amino benzene sulphonic acid, $C_6H_4NH_2SO_3H$, is the most important of the three sulphonic acids derived from aniline. It is made by the " baking " process.

Experiment.—To prepare sulphanilic acid.

Place 30 c.c. of aniline in a 250 c.c. round-bottomed flask and add cautiously 50 c.c. of concentrated sulphuric acid a little at a time with constant shaking. Heat the mixture to 200° C. in an oil bath (i.e. " baking ") for five hours until a test portion when dissolved in water gives no precipitate (of aniline) when made alkaline with caustic soda. The product is then poured into cold water; the sulphanilic acid is precipitated as a grey crystalline mass. Filter, wash and recrystallize from hot water. If the precipitate is discoloured add a little animal charcoal and filter hot, using a steam funnel. The acid separates out on cooling; filter off and dry in the air.

The reactions may be represented as follows:

Aniline   Aniline acid   Phenyl
               sulphate   sulphonamic acid

o-sulphanilic acid   *p*-sulphanilic acid
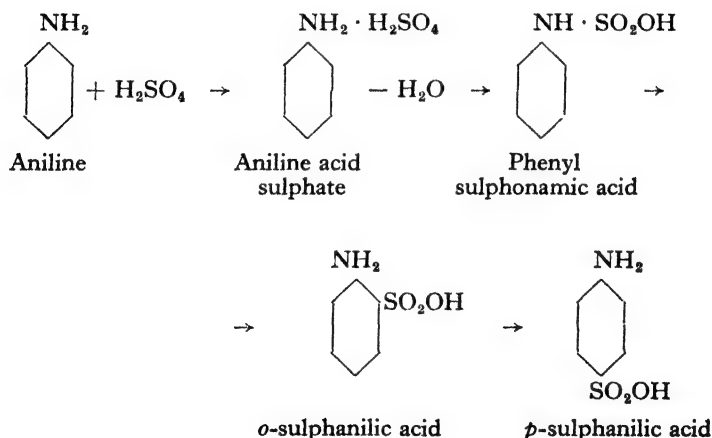
The formation of sulphanilic acid from aniline is a reaction known as **Sulphonation.**

Properties.—Colourless monoclinic crystals containing two molecules of water of crystallization. Sparingly soluble in cold water but more readily soluble in hot water.

Reactions.—1. It is a strong acid, decomposing carbonates and forming salts which have a neutral reaction:

Sodium sulphanilate
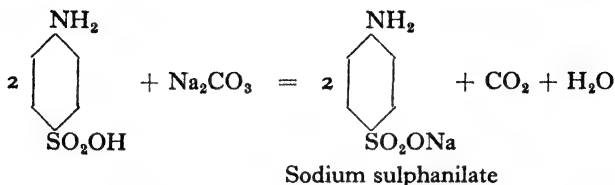
2. When fused with caustic soda aniline is produced, not *p*-amino-phenol:
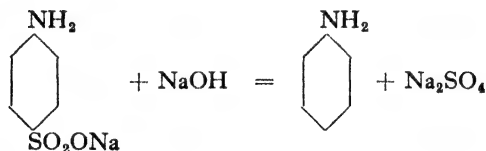
Sulphanilic acid is used in the manufacture of azo-dyes.

For example, methyl orange is formed by first diazotizing sulphanilic acid and then treating the resulting compound with dimethylaniline:

| Diazotized sulphanilic acid | Dimethyl-aniline | Helianthin, *p*-dimethyl-amino-azo-benzene *p*-sulphonic acid |
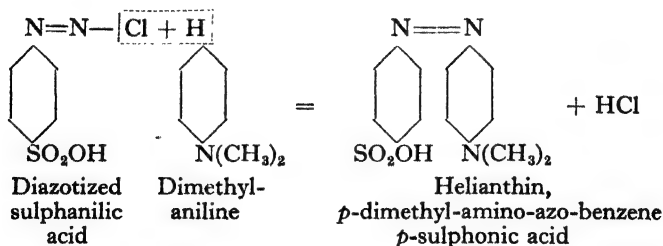
Methyl orange is the sodium salt of this acid, formed by replacing the hydrogen atom of the —SO_2OH group with sodium by treatment with caustic soda.

Substitution in the Benzene Series.

From the various derivatives of aniline already mentioned it will be observed that ortho-, meta- and para-substitution products can be obtained and according to conditions one or other of these products predominates.

The group already present in a mono-substitution product of benzene, e.g. —NH_2 in aniline, exerts a directing influence on the position taken up by a second group capable of directly displacing hydrogen in the nucleus. This influence is exerted independently of the nature of the group introduced and is expressed by certain rules known as the " rules of the constancy of substitution type " or the " rules of substitution in the benzene series ". These are given below.

A. Substitution in the **ortho-** or **para-** position is generally caused by the following groups (R is a mono-valent radicle):

$$Cl, Br, I, OH, OR, OCO \cdot CH_3;$$

$$NH_2, NHR, NR_2, NH \cdot COCH_3;$$
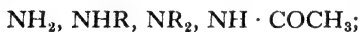
CH_3 or other alkyl group or substituted group, such as
$$CH_2Cl, CH_2NH_2, CH_2Cl, CH_2SO_2OH, CH_2COOH;$$

$$CH{=}CH \cdot COOH; C{\equiv}C \cdot COOH.$$
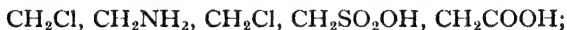
The main product is the **para**-compound, with smaller amounts of ortho- and little or no meta- compound.

Example 1.—When chlorine acts upon cold toluene in diffused daylight in the presence of a halogen carrier (iodine, iron wire, aluminium foil, &c.) ortho- and para- chlorotoluenes and no meta- compound are produced. The —CH_3

mono-substituted group directs the chlorine to the ortho-
and para-positions:

Toluene   o-chlorotoluene   p-chlorotoluene
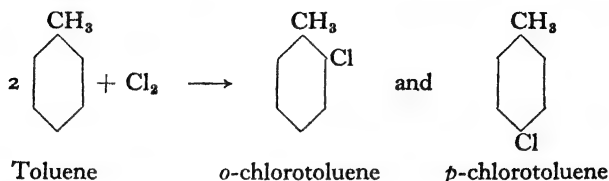
Example 2.—Nitration of phenol with dilute nitric acid
produces about equal quantities of ortho- and para-nitro-
phenol, which are separated by distillation in steam, the
ortho-product being volatile. No meta-compound is formed.
The —OH group directs the —NO_2 group to the ortho-
and para-positions.

Phenol   o-nitrophenol   p-nitrophenol
(m. pt. 42° C.)   (m. pt. 44·0° C.)   (m. pt. 114° C.)
b. pt. 182° C.)   (b. pt. 215° C.)
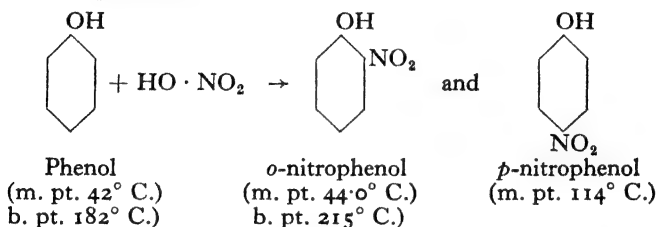
B. Substitution in the **meta** position is generally caused
by the following groups:

COOH, CN, NO_2, $CONH_2$, SO_2OH, CHO, CRO, CCl_3
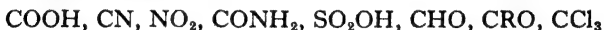
Example.—When benzoic acid is treated with nitric acid
at 0° C. 81 per cent of the product consists of the meta-
compound (18 per cent ortho, 1 per cent para). The
—COOH group directs the —NO_2 to the meta position:

Benzoic   m-nitrobenzoic
acid   acid
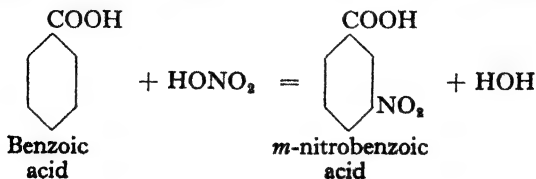
Attempts have been made to classify the two sets of groups. Crum Brown and Gibson's classification is as follows:

A. **Ortho-** and **para-**compounds are formed if the radicle already present in the benzene ring forms a compound with hydrogen which cannot be directly oxidized to the hydroxy-compound, e.g.

Substituent	Hydrogen compound	Hydroxy-compound
—Cl	HCl	HOCl
—CH_3	CH_4	CH_3OH
—NH_2	NH_3	NH_2OH
—OH	HOH	$HO \cdot OH$

The hydroxy-compound CH_3OH is an exception, as CH_4 can be directly oxidized to it.

B. **Meta-**compounds are formed when the radicle already present forms a hydrogen compound which is oxidized directly to the hydroxy-compound, e.g.

Substituent	Hydrogen compound	Hydroxy-compound
—CHO	HCHO	HCOOH
—NO_2	HNO_2	HNO_3
—$COCH_3$	CH_3CHO	CH_3COOH

Usually, however, all three isomerides are formed at the same time, but the relative proportions depend on:
(a) the substituent actually present,
(b) the substituent introduced,
(c) conditions of the experiment, such as temperature, reagent employed, catalysts used.

For example, the effect of temperature may be illustrated by the action of concentrated sulphuric acid on toluene; the following percentages of toluene sulphonic acids are obtained:

Temperature	Para	Ortho	Meta	Formula
$0°$	53·5	42·7	3·8	$C_6H_4 \bigg\langle \begin{matrix} CH_3 \\ SO_2OH \end{matrix}$
$100°$ C.	72·5	17·5	10·1	

As an illustration of the effect of the reagent employed, we have the nitration of acetanilide with

(*a*) fuming nitric acid: mixture of ortho- and para-compounds;

(*b*) nitric acid in the presence of concentrated sulphuric acid: about 95 per cent para-compound;

(*c*) nitrogen pentoxide in the presence of acetic anhydride: almost entirely ortho-compound.

$$C_6H_5NH \cdot CO \cdot CH_3 + HNO_3 = C_6H_4(NO_2)NH \cdot CO \cdot CH_3 + H_2O$$
Nitro-acetanilide
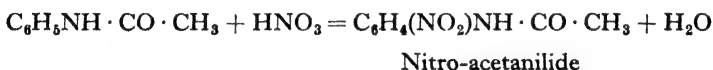
For further information on this subject larger works on Organic Chemistry must be consulted.

The Toluidines, $CH_3 \cdot C_6H_4 \cdot NH_2$.

Just as aniline can be obtained by substituting an amino-group for a hydrogen atom in the benzene nucleus, so the homologues of benzene can form amino-derivatives.

Toluene can form three amino-toluenes, which are known as toluidines. The ortho- and para-compounds are formed by direct nitration of toluene, followed by the reduction of the nitro-compounds produced. The meta-

compound is prepared by the reduction of *m*-nitrotoluene or *m*-nitrobenzaldehyde:

(HNO₃)

o-nitrotoluene

o-toluidine
(Liquid, b. pt. 197° C.)

Toluene

CrO₂Cl₂

p-nitrotoluene

p-toluidine
(Solid, m. pt. 45° C.,
b. pt. 198° C.)

Benzaldehyde   m-nitrobenzaldehyde   m-toluidine
(liquid, b. pt. 199° C.)
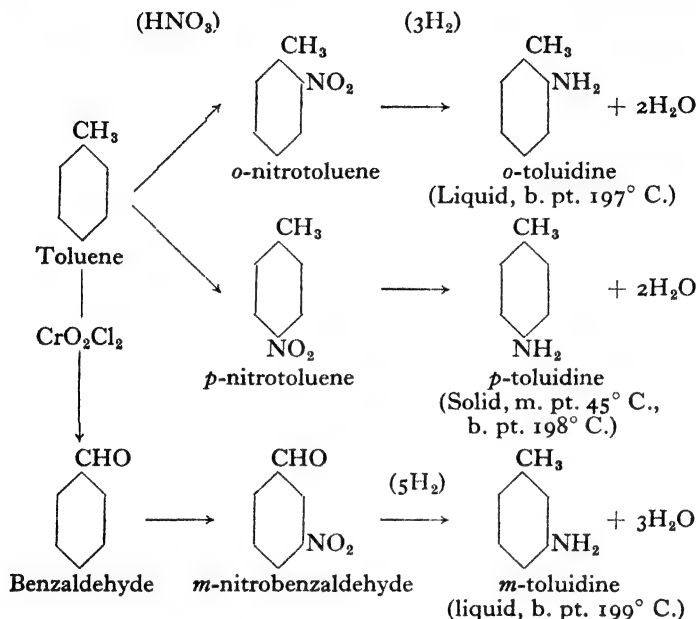
The toluidines are weak bases almost insoluble in water. They resemble aniline in their properties. They are used to a large extent in the preparation of dyestuffs.

Aniline forms an azo-dye with a diazonium salt, coupling taking place in the para-position.

Aniline   Benzene
                   diazonium
                   chloride

p-amino-azo-benzene
(an azo-dye, the hy-
drochloride of which
is known as aniline
yellow)
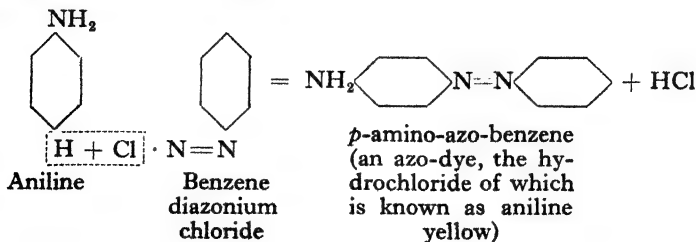
This is a general reaction when the ortho- and para-positions are free. Thus phenol gives a compound of similar type, known as hydroxy-azo-benzene, $C_6H_5 \cdot N : N \cdot C_6H_4 \cdot OH$.

Para-toluidine forms an azo-dye with a diazonium salt, but the coupling takes place in the ortho-position relative to the —NH_2 group:

Toluidine   2-amino-5-methyl-azo-benzene
(an azo-dye)
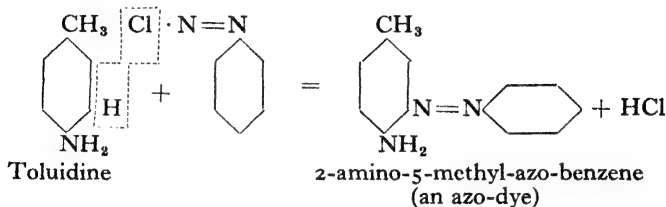
This is a general reaction when the para-position is occupied. In the same way, para-cresol, $C_6H_4OH \cdot CH_3$, gives an azo-dye. These azo-dyes are used as tests for primary amines with the —NH_2 group in the nucleus.

Diazo-Compounds

Diazotization, as has been mentioned, is the name given to the reaction by which primary aromatic amino-compounds can be converted into diazo-compounds by the action of nitrous acid (p. 450). The nitrous acid is generated in situ by treating an alkali nitrite with hydrochloric acid. In order to obtain the diazo-salt it is important that the temperature should be kept at 0° C.; on no account must it rise above 10° C.

$$C_6H_5NH_2 \cdot HCl + NaNO_2 + HCl = C_6H_5N{=}N \cdot Cl + NaCl + 2H_2O$$

Aniline   Diazobenzene
hydrochloride   chloride

$$C_6H_4(CH_3)NH_2 \cdot HCl + NaNO_2 + HCl$$

p-toluidine
hydrochloride

$$= C_6H_4CH_3 \cdot N{=}N \cdot Cl + NaCl + 2H_2O$$

p-toluene
diazonium chloride

These compounds are salts of strong bases. Diazobenzene chloride is derived from diazobenzene hydrate, which can be prepared by the action of moist silver oxide on a diazo-salt:

$$C_6H_5N = N \cdot \boxed{Cl + Ag} \cdot OH = C_6H_5N = N \cdot OH + AgCl$$
<div align="center">Diazobenzene
hydrate</div>

Diazo-salts may be regarded as substituted ammonium salts, hence the name diazonium.

The free bases are soluble in water, forming strongly alkaline solutions. The diazo-salts are colourless crystalline substances also soluble in water. All diazo-compounds are very unstable, and when obtained in the dry state are liable to explode violently. The diazonium salts and diazotates are neutral in solution. Aliphatic primary amines and secondary and tertiary aromatic amines do not form diazo-salts.

The diazonium compounds are of considerable importance in organic synthesis. Their more important reactions and the products formed are briefly described below:

Reactions.—1. **Phenols:** by heating the aqueous solution of the diazo-compound:

$$C_6H_5N : N \cdot Cl + HOH = C_6H_5OH + HCl + N_2$$
<div align="center">Phenol</div>

$$CH_3 \cdot C_6H_4 \cdot N : N \cdot SO_4H + HOH = CH_3 \cdot C_6H_4OH + H_2SO_4 + N_2$$

<div align="center">

o-, *m*-, *p*-
toluene diazonium sulphates   *o*-, *m*-, *p*-
cresols

</div>

This reaction indicates how a diazonium group, e.g. —N : N · Cl, may be replaced by a hydroxyl group.

2. **Benzene and its Homologues:** by heating an alcoholic solution of the diazo-compound. During the

reaction the alcohol is oxidized to acetaldehyde, liberating hydrogen, which then reduces the diazo-salt.

$$CH_3 \cdot CH_2OH = CH_3CHO + 2H,$$
$$C_6H_5 \cdot N : N \cdot Cl + 2H = C_6H_6 + HCl + N_2.$$
<div align="center">Benzene</div>
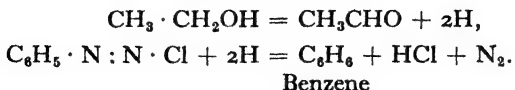
Here the diazonium group is replaced by a hydrogen atom.

3. **Phenolic Ethers**: also by heating an alcoholic solution of the diazo-compound, as in the previous reaction. This is the main reaction, benzene being formed in small quantities only.
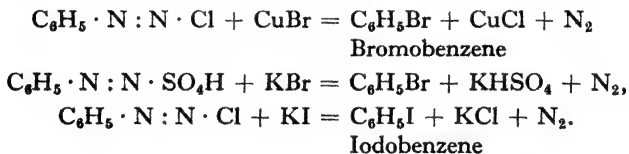
$$C_6H_5 \cdot N : N \cdot Cl + C_2H_5OH = C_6H_5 \cdot O \cdot C_2H_5 + HCl + N_2$$
<div align="center">Phenyl ethyl ether
(Phenetol)</div>
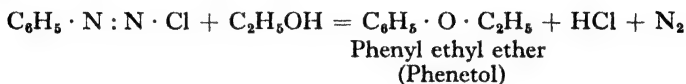
The diazonium group in this reaction is replaced by an ethoxy ($-OC_2H_5$) group or by other similar groups.

4. **Halogen Derivatives and Cyanides.** (*a*) *Sandmeyer's Reaction*: by warming the diazonium salt with the appropriate cuprous salt and acid (p. 402).

(*b*) *Gattermann's Method*: by heating with copper powder and the alkali halide (for the iodide no catalyst is needed).

$$C_6H_5 \cdot N : N \cdot Cl + CuBr = C_6H_5Br + CuCl + N_2$$
<div align="center">Bromobenzene</div>

$$C_6H_5 \cdot N : N \cdot SO_4H + KBr = C_6H_5Br + KHSO_4 + N_2,$$
$$C_6H_5 \cdot N : N \cdot Cl + KI = C_6H_5I + KCl + N_2.$$
<div align="center">Iodobenzene</div>

Iodobenzene is a mobile liquid, b. pt. 188° C. The halogen in the nucleus is firmly bound and cannot be replaced by OH, NH_2, &c. (contrast aliphatic compounds).

5. **Phenylhydrazine**: by reduction with tin and concentrated hydrochloric acid:

$$C_6H_5 \cdot N : N \cdot Cl + 4H = C_6H_5NH \cdot NH_2 + HCl$$
<div align="center">Phenylhydrazine</div>
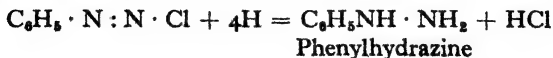
This compound when pure forms colourless crystals,

m. pt. 19° C., but is usually obtained as a dark brown oil. It is used to identify aldehydes, ketones and certain sugars (aldoses and ketoses) (pp. 172, 182, 352), and in the manufacture of antipyrine (used in medicine as a febrifuge).

6. **Sulphides** and **Thiophenols:** by the action of hydrogen sulphide:

$$2C_6H_5 \cdot N : N \cdot Cl + H_2S = C_6H_5 \cdot S \cdot C_6H_5 + 2HCl + 2N_2$$
<div align="center">Diphenyl sulphide</div>

$$C_6H_5 \cdot N : N \cdot Cl + H_2S = C_6H_5 \cdot SH + HCl + N_2$$
<div align="center">Thiophenol</div>

7. **Diazotates:** by the action of concentrated alkalis on the diazonium compounds:

$$C_6H_5 \cdot N : N \cdot Cl + KOH = C_6H_5N : N \cdot OK + HCl$$
<div align="center">Potassium
diazotate</div>

8. **Azo-dyes** (pp. 450, 468) are obtained by coupling a diazo-compound with various aromatic amino-, phenolic, or sulphonic compounds, e.g.

Benzene diazonium chloride   *p*-cresol   2-hydroxy-5-methyl azo-benzene
(Azo-dye in ortho- position, cf. p. 469)
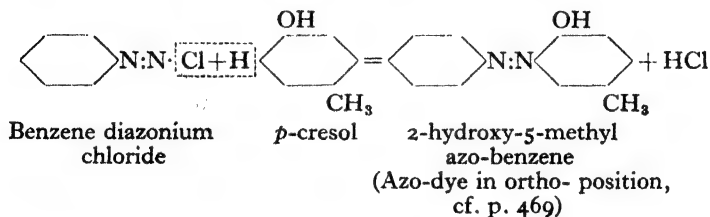
Most of these dyes are reddish (e.g. Chrysoidine) brown (e.g. Bismarck brown) or yellow (e.g. Resorcin yellow).

From these reactions it is abundantly clear that a considerable number of substitution products of benzene and its homologues can be prepared, as the —NH$_2$ group can be replaced by —OH, —OC$_2$H$_5$, H, Cl, Br, I, —CN and hence —COOH, &c.

Constitution of the Diazo-Compounds.

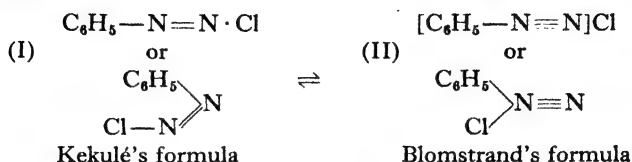The diazo-compounds exhibit tautomerism, that is, their constitutions may be expressed by two different structures:

$$\text{(I)} \quad \begin{array}{c} C_6H_5 - N = N \cdot Cl \\ \text{or} \\ \underset{Cl-N}{\overset{C_6H_5}{\diagdown}} N \\ \text{Kekulé's formula} \end{array} \rightleftharpoons \text{(II)} \quad \begin{array}{c} [C_6H_5 - N = N]Cl \\ \text{or} \\ \underset{Cl}{\overset{C_6H_5}{\diagdown}} N \equiv N \\ \text{Blomstrand's formula} \end{array}$$
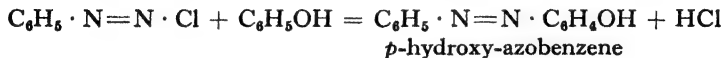
In the first formula both nitrogen atoms are trivalent, whereas in the second formula one nitrogen atom is pentavalent and the other trivalent. Both formulæ are substantiated by the products formed with various reagents and by the fact that, like amphoteric compounds, the diazocompounds can react with both strong acids and strong bases.

Arguments for Kekulé's formula.

1. The reduction of diazonium salts to hydrazines, e.g.

$$C_6H_5 \cdot N = N \cdot Cl + 2H_2 = \underset{\text{Phenylhydrazine}}{C_6H_5 \cdot NH \cdot NH_2} + HCl$$

2. The conversion of diazonium salts into azo-dyes, e.g.

$$C_6H_5 \cdot N = N \cdot Cl + C_6H_5OH = \underset{p\text{-hydroxy-azobenzene}}{C_6H_5 \cdot N = N \cdot C_6H_4OH} + HCl$$

Arguments for Blomstrand's Formula.

1. The close resemblance between diazonium salts and ammonium salts:

$$\underset{Cl}{\overset{C_6H_5}{\diagdown}} N \equiv N; \qquad \underset{Cl}{\overset{H}{\diagdown}} N \equiv H_3; \qquad \underset{Cl}{\overset{C_6H_5}{\diagdown}} N \equiv (CH_3)_3$$

$$\underset{\substack{\text{Ammonium} \\ \text{chloride}}}{}$$
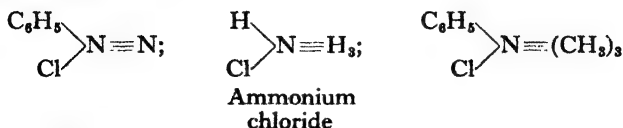
2. The ready and simpler explanation of the formation of diazonium salts, e.g.

$$
\begin{array}{c}
C_6H_5 \\
\diagdown \\
N - \\
Cl \diagup
\end{array}
\begin{array}{c}
\diagup \; \overline{H \quad\quad H-O} \\
\overline{H} \; + \\
\diagdown \; \overline{H \quad\quad O} = N
\end{array}
=
\begin{array}{c}
C_6H_5 \\
\diagdown \\
\diagup N \equiv N + 2H_2O \\
Cl
\end{array}
$$

<center>Aniline   Diazobenzene
hydrochloride   chloride</center>
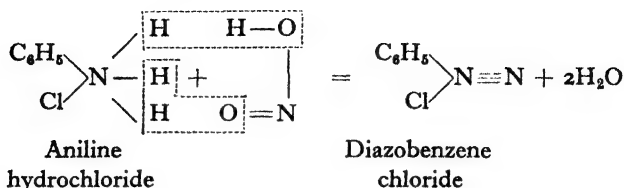
3. The readiness with which nitrogen is evolved on reduction, hydrolysis, &c., suggests that in addition to the nitrogen atoms being directly linked together one of these nitrogen atoms is at the end of the side chain:

$$
\begin{array}{c}
C_6H_5 \\
\diagdown \\
\diagup N \equiv N + \\
Cl
\end{array}
\begin{array}{c}
O - H \\
| \\
H
\end{array}
= C_6H_5OH + HCl + N_2
$$

4. The formation of mono-substituted products, as illustrated by the characteristic reactions described previously.

Notes.—(a) Blomstrand's formula is now generally accepted.

(b) Kekulé's formula, however, has been adopted in the various equations for convenience.

QUESTIONS

1. If you were provided with an organic compound containing nitrogen, what experiments would you carry out to determine in what form or combination the nitrogen existed?

<div align="right">(<i>Phar. Chem. Qual.</i>)</div>

2. A certain liquid is known to be a hydrocarbon. Describe fully the tests you would apply to it to ascertain whether it belonged to the aliphatic group or the aromatic group.

In what chemical properties does an aromatic amine, such as aniline, differ from an aliphatic amine, such as methylamine?

<div align="right">(<i>Civil Service: Executive Group.</i>)</div>

3. Classify the reactions of sulphuric acid, illustrating your answer by reference to its effects on (*a*) water, (*b*) ethylene, (*c*) aniline, (*d*) benzene, (*e*) alcohol, (*f*) potassium iodide, (*g*) potassium dichromate. State the conditions under which the reactions occur. (*Oxford Higher School Cert.*)

4. How is benzene obtained? Describe its properties and reactions, and state how it may be converted into (*a*) toluene, (*b*) aniline, (*c*) benzoic acid. (*Chemists and Druggists Qual.*)

5. Write an account of the properties of those organic compounds which contain either the hydroxyl (—OH) group or the amino (—NH$_2$) group, and show how the character of the group you choose is conditioned by the nature of the other atoms or groups present in the molecule.

How would you introduce one of these groups into (*a*) benzene and (*b*) propane? (*Civil Service: Executive Group.*)

6. Write equations for *three* reactions by which monoethylamine is produced.

Write a comparative account of the behaviour of ethylamine, diethylamine and aniline when treated with (*a*) water, (*b*) dilute sulphuric acid, (*c*) nitrous acid.

(*Cambridge Higher School Cert.*)

7. Explain the reactions involved in the preparation of (*a*) picric acid from phenol, (*b*) oleic acid from olive oil, (*c*) phenol from aniline, (*d*) phenol from benzene.

(*Chemists and Druggists Qual.*)

8. Distinguish between amines, amides and amino-acids. Describe the action, if any, of (*a*) nitrous acid, (*b*) aqueous sodium hydroxide, (*c*) acetyl chloride, on each class of substance.

(*Cambridge Higher School Cert.*)

9. Describe, giving essential details, the reactions which take place when nitrobenzene is reduced under various conditions.

(*Phar. Chem. Qual.*)

10. Describe briefly the preparation of the following: aniline from nitrobenzene, lactic acid from cane sugar, phenol from benzene, chloroform from acetone, glucose from starch.

11. Explain by means of two examples in each case the following reactions: nitration, sulphonation, diazotization, acetylation and polymerization. (*Chemists and Druggists Qual.*)

12. Explain briefly the steps you would take to convert (*a*) benzene into aniline, (*b*) aniline into phenol, (*c*) benzoic acid into phenol. Write structural formulæ for each of these substances.

13. Explain the " diazo " reaction. Illustrate its application to the preparation of (*a*) phenols, (*b*) hydrocarbons, (*c*) halogen substitution products. (*Chemists and Druggists Qual.*)

14. Starting with benzene, indicate briefly how each of the following derivatives may be obtained: phenol, salicyclic. acid, benzaldehyde, benzoic acid.

15. Indicate the most important commercial source of benzene. Starting with benzene, how would you prepare in the laboratory pure specimens of (*a*) aniline, and (*b*) phenol? How may benzene be obtained from phenol?

(*London Higher School Cert.*)

16. Discuss briefly the chemistry of aromatic hydrocarbons with special reference to the formation of derivatives by addition and by substitution. Explain the directional influence of the following groups: —CH$_3$, —NO$_2$, —COOH, —OH.

(*Chemists and Druggists Qual.*)

17. What radical characterizes an ester, an amide, an alcohol, an amine, a ketone, an aldehyde, a hydrocarbon, a diazo-compound, a nitrile, and an organic acid? (*Inst. of Patent Agents.*)

18. Write a general account of the part played by either nitrogen or the halogens in organic chemistry.

(*Inst. of Patent Agents.*)

The Grignard Reagents

The Grignard reagents, named after their discoverer, are extremely important in organic chemistry. They have the general formula:

$$R—Mg—X$$

where R is a monovalent organic radicle and X a halogen atom. They may be divided into two groups:
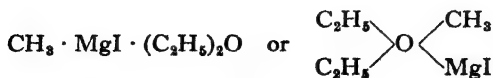
I. Aliphatic compounds, represented by:

> Methyl magnesium chloride, $CH_3 \cdot Mg \cdot Cl$,
> Methyl magnesium bromide, $CH_3 \cdot Mg \cdot Br$.

II. Aromatic compounds, represented by:

> Phenyl magnesium bromide, $C_6H_5 \cdot Mg \cdot Br$,
> Benzyl magnesium chloride, $C_6H_5 \cdot CH_2 \cdot Mg \cdot Cl$.

The aliphatic Grignard reagents are prepared by dissolving dry powdered magnesium in the calculated amount of dry alkyl halide in dry ether. It is absolutely essential that moisture should be absent. When the solution is evaporated in an atmosphere of hydrogen, a white crystalline solid is left, consisting of the Grignard reagent combined with ether either as " ether of crystallization " or as an oxonium compound (a derivative of tetravalent oxygen), e.g.

$$CH_3 \cdot MgI \cdot (C_2H_5)_2O \quad \text{or} \quad \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!\diagup\!\!\diagdown O \diagdown\!\!\diagup \begin{matrix} CH_3 \\ MgI \end{matrix}$$

This additive compound is employed in organic reactions, as the ether apparently does not interfere with the reactions.
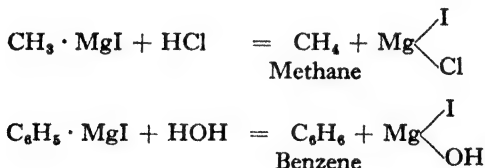
The aromatic Grignard reagents are made by adding dry magnesium powder to aromatic halogen derivatives in dry ethereal solutions. It is immaterial whether the halogen is in the nucleus or in the side-chain.

The aliphatic reagents are fairly stable and can be used directly. The aromatic reagents are also stable, but they react much more effectively on the addition of a drop of methyl iodide or a crystal of iodine.

The Grignard reagents are of considerable importance as synthetic reagents in the preparations of the following groups of compounds, some of which are illustrated in the reactions outlined below:

Paraffins; Olefines; Primary, Secondary and Tertiary alcohols; Ethers; Aldehydes; Ketones; Acids; Phenols, &c.

Reactions.—1. **Methane** and **Benzene**: by the action of water or hydrochloric acid on the simplest Grignard reagents:

$$CH_3 \cdot MgI + HCl = \underset{\text{Methane}}{CH_4} + Mg\begin{cases} I \\ Cl \end{cases}$$

$$C_6H_5 \cdot MgI + HOH = \underset{\text{Benzene}}{C_6H_6} + Mg\begin{cases} I \\ OH \end{cases}$$
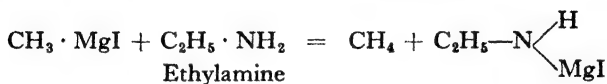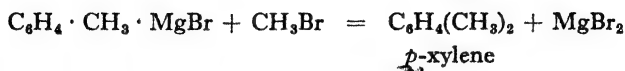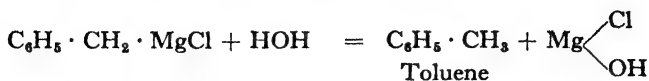
2. **Saturated Hydrocarbons.**—Grignard reagents react with compounds containing a hydroxyl group (e.g. alcohols, water), with alkyl halides, and with primary and secondary amines to form saturated hydrocarbons:

$$CH_3 \cdot MgI + C_2H_5OH = \underset{\text{Methane}}{CH_4} + C_2H_5 \cdot OMgI$$
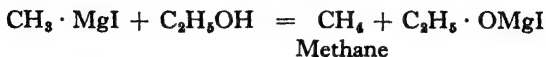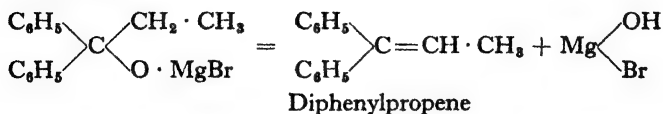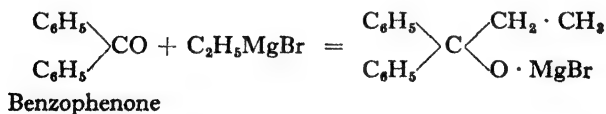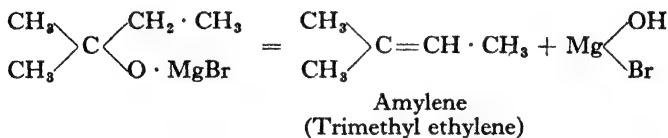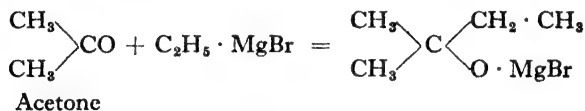
(This reaction is used to estimate the number of hydroxyl

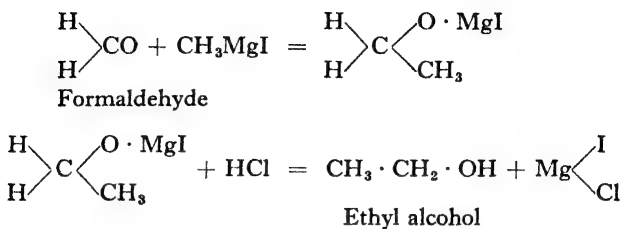groups present in an organic compound, the volume of methane evolved being measured.)

$$C_6H_5 \cdot CH_2 \cdot MgCl + HOH \quad = \quad C_6H_5 \cdot CH_3 + Mg{<}^{Cl}_{OH}$$
$$\text{Toluene}$$

$$C_6H_4 \cdot CH_3 \cdot MgBr + CH_3Br \quad = \quad C_6H_4(CH_3)_2 + MgBr_2$$
$$\underset{}{p}\text{-xylene}$$

$$CH_3 \cdot MgI + C_2H_5 \cdot NH_2 \quad = \quad CH_4 + C_2H_5{-}N{<}^{H}_{MgI}$$
$$\text{Ethylamine}$$

$$CH_3 \cdot MgI + (C_2H_5)_2 \cdot NH \quad = \quad CH_4 + (C_2H_5)_2 : N{-}MgI$$
$$\text{Diethylamine}$$

3. **Olefines:** by the action of the appropriate Grignard reagent on ketones:

$$\overset{CH_3}{\underset{CH_3}{>}}CO + C_2H_5 \cdot MgBr \ = \ \overset{CH_3}{\underset{CH_3}{>}}C{<}^{CH_2 \cdot CH_3}_{O \cdot MgBr}$$
$$\text{Acetone}$$

$$\overset{CH_3}{\underset{CH_3}{>}}C{<}^{CH_2 \cdot CH_3}_{O \cdot MgBr} \ = \ \overset{CH_3}{\underset{CH_3}{>}}C{=}CH \cdot CH_3 + Mg{<}^{OH}_{Br}$$
$$\text{Amylene}$$
$$\text{(Trimethyl ethylene)}$$

$$\overset{C_6H_5}{\underset{C_6H_5}{>}}CO + C_2H_5MgBr \ = \ \overset{C_6H_5}{\underset{C_6H_5}{>}}C{<}^{CH_2 \cdot CH_3}_{O \cdot MgBr}$$
$$\text{Benzophenone}$$

$$\overset{C_6H_5}{\underset{C_6H_5}{>}}C{<}^{CH_2 \cdot CH_3}_{O \cdot MgBr} \ = \ \overset{C_6H_5}{\underset{C_6H_5}{>}}C{=}CH \cdot CH_3 + Mg{<}^{OH}_{Br}$$
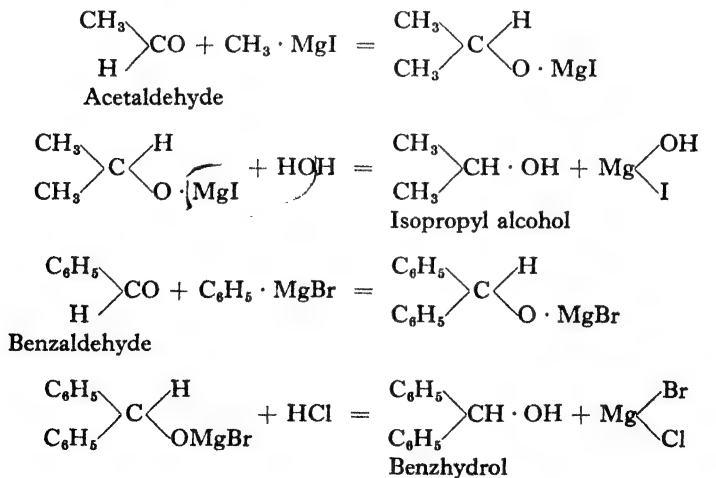$$\text{Diphenylpropene}$$

4. **Primary Alcohols:** by the action of a Grignard

reagent on formaldehyde. The additive product first formed is treated with dilute acid:

$$\underset{\text{Formaldehyde}}{\overset{H}{\underset{H}{>}}CO} + CH_3MgI = \overset{H}{\underset{H}{>}}C\overset{O \cdot MgI}{\underset{CH_3}{<}}$$

$$\overset{H}{\underset{H}{>}}C\overset{O \cdot MgI}{\underset{CH_3}{<}} + HCl = \underset{\text{Ethyl alcohol}}{CH_3 \cdot CH_2 \cdot OH} + Mg\overset{I}{\underset{Cl}{<}}$$
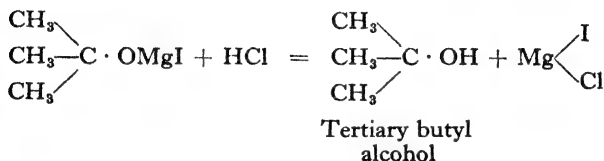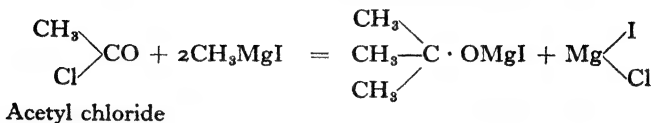
5. **Secondary Alcohols:** by the action of the Grignard reagent on aldehydes other than formaldehyde in dry ethereal solution; the additive product formed is treated with water or dilute acids:
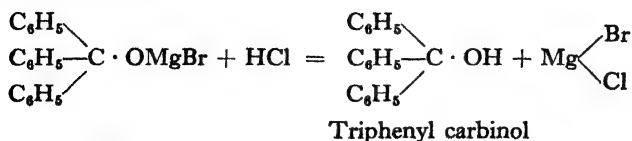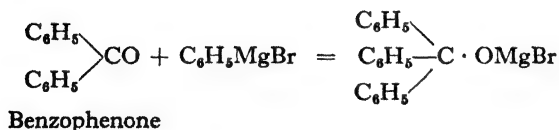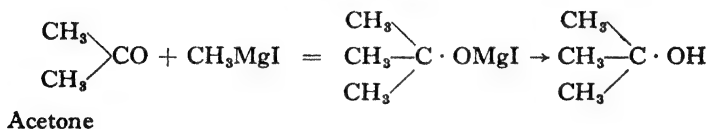
$$\underset{\text{Acetaldehyde}}{\overset{CH_3}{\underset{H}{>}}CO} + CH_3 \cdot MgI = \overset{CH_3}{\underset{CH_3}{>}}C\overset{H}{\underset{O \cdot MgI}{<}}$$

$$\overset{CH_3}{\underset{CH_3}{>}}C\overset{H}{\underset{O \cdot MgI}{<}} + HOH = \underset{\text{Isopropyl alcohol}}{\overset{CH_3}{\underset{CH_3}{>}}CH \cdot OH} + Mg\overset{OH}{\underset{I}{<}}$$

$$\underset{\text{Benzaldehyde}}{\overset{C_6H_5}{\underset{H}{>}}CO} + C_6H_5 \cdot MgBr = \overset{C_6H_5}{\underset{C_6H_5}{>}}C\overset{H}{\underset{O \cdot MgBr}{<}}$$

$$\overset{C_6H_5}{\underset{C_6H_5}{>}}C\overset{H}{\underset{OMgBr}{<}} + HCl = \underset{\text{Benzhydrol}}{\overset{C_6H_5}{\underset{C_6H_5}{>}}CH \cdot OH} + Mg\overset{Br}{\underset{Cl}{<}}$$

Phenyl methyl carbinol, $\overset{C_6H_5}{\underset{CH_3}{>}}CH{\cdot}OH$, is similarly obtained from benzaldehyde and CH_3MgBr.

6. **Tertiary Alcohols**: by the action of the Grignard reagent on the following compounds, and subsequent treatment of the product with hydrochloric acid.
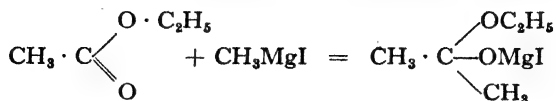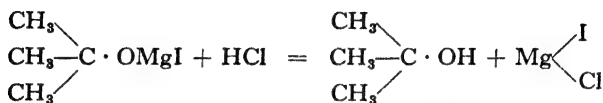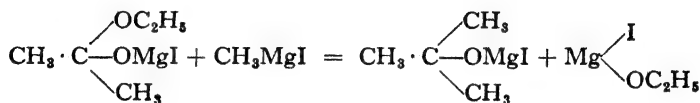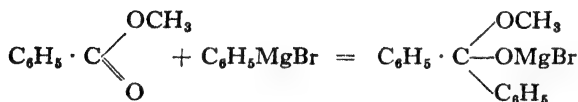
A. Acid Chlorides

$$\begin{array}{c} CH_3 \\ \diagdown \\ Cl \diagup \end{array} CO + 2CH_3MgI \;=\; \begin{array}{c} CH_3 \\ \diagdown \\ CH_3{-}C \cdot OMgI \\ \diagup \\ CH_3 \end{array} + Mg\begin{array}{c} I \\ \diagdown \\ Cl \end{array}$$

Acetyl chloride

$$\begin{array}{c} CH_3 \\ \diagdown \\ CH_3{-}C \cdot OMgI \\ \diagup \\ CH_3 \end{array} + HCl \;=\; \begin{array}{c} CH_3 \\ \diagdown \\ CH_3{-}C \cdot OH \\ \diagup \\ CH_3 \end{array} + Mg\begin{array}{c} I \\ \diagdown \\ Cl \end{array}$$

Tertiary butyl
alcohol

B. Ketones

$$\begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \diagup \end{array} CO + CH_3MgI \;=\; \begin{array}{c} CH_3 \\ \diagdown \\ CH_3{-}C \cdot OMgI \\ \diagup \\ CH_3 \end{array} \rightarrow \begin{array}{c} CH_3 \\ \diagdown \\ CH_3{-}C \cdot OH \\ \diagup \\ CH_3 \end{array}$$

Acetone

$$\begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5 \diagup \end{array} CO + C_6H_5MgBr \;=\; \begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5{-}C \cdot OMgBr \\ \diagup \\ C_6H_5 \end{array}$$

Benzophenone

$$\begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5{-}C \cdot OMgBr \\ \diagup \\ C_6H_5 \end{array} + HCl \;=\; \begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5{-}C \cdot OH \\ \diagup \\ C_6H_5 \end{array} + Mg\begin{array}{c} Br \\ \diagdown \\ Cl \end{array}$$

Triphenyl carbinol

C. Esters of Organic Acids

$$CH_3 \cdot C\!\!\begin{array}{c} O \cdot C_2H_5 \\ \\ O \end{array} + CH_3MgI = CH_3 \cdot C\!\!\begin{array}{c} OC_2H_5 \\ -OMgI \\ CH_3 \end{array}$$

Ethyl acetate

$$CH_3 \cdot C\!\!\begin{array}{c} OC_2H_5 \\ -OMgI \\ CH_3 \end{array} + CH_3MgI = CH_3 \cdot C\!\!\begin{array}{c} CH_3 \\ -OMgI \\ CH_3 \end{array} + Mg\!\!\begin{array}{c} I \\ OC_2H_5 \end{array}$$

$$\begin{array}{c} CH_3 \\ CH_3 \!-\! C \cdot OMgI \\ CH_3 \end{array} + HCl = \begin{array}{c} CH_3 \\ CH_3 \!-\! C \cdot OH \\ CH_3 \end{array} + Mg\!\!\begin{array}{c} I \\ Cl \end{array}$$

Trimethyl carbinol

$$C_6H_5 \cdot C\!\!\begin{array}{c} OCH_3 \\ \\ O \end{array} + C_6H_5MgBr = C_6H_5 \cdot C\!\!\begin{array}{c} OCH_3 \\ -OMgBr \\ C_6H_5 \end{array}$$

Methyl benzoate

$$C_6H_5 \cdot C\!\!\begin{array}{c} OCH_3 \\ -OMgBr \\ C_6H_5 \end{array} + C_6H_5MgBr = C_6H_5 \cdot C\!\!\begin{array}{c} C_6H_5 \\ -OMgBr \\ C_6H_5 \end{array} + Mg\!\!\begin{array}{c} Br \\ OCH_3 \end{array}$$

$$\begin{array}{c} C_6H_5 \\ C_6H_5 \!-\! C \cdot OMgBr \\ C_6H_5 \end{array} + HCl = \begin{array}{c} C_6H_5 \\ C_6H_5 \!-\! C \cdot OH \\ C_6H_5 \end{array} + Mg\!\!\begin{array}{c} Cl \\ Br \end{array}$$

Triphenyl carbinol

D. Amides

$$CH_3 \diagdown CO + CH_3MgI = CH_3 \diagdown C \diagup CH_3$$
$$NH_2 \diagup \qquad\qquad\qquad NH_2 \diagup \diagdown OMgI$$
Acetamide

$$CH_3 \diagdown C \diagup CH_3 + CH_3MgI = CH_3 \diagdown C \diagup CH_3 + H—N \diagup H$$
$$NH_2 \diagup \diagdown OMgI \qquad\qquad CH_3 \diagup \diagdown OMgI \qquad\qquad \diagdown MgI$$

$$H—N \diagup H + HCl = NH_3 + Mg \diagup I$$
$$\diagdown MgI \qquad\qquad\qquad\qquad \diagdown Cl$$

$$CH_3 \diagdown$$
$$CH_3—C \cdot OMgI + HCl = CH_3—C \cdot OH + Mg \diagup I$$
$$CH_3 \diagup \qquad\qquad\qquad CH_3 \diagup \qquad\qquad \diagdown Cl$$
Tertiary butyl alcohol
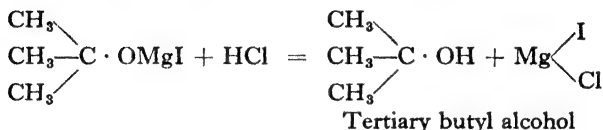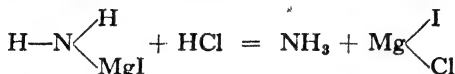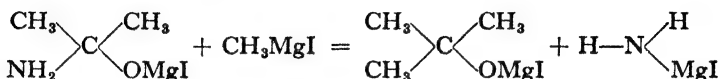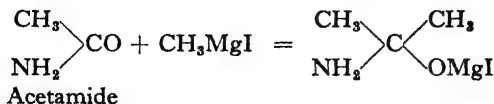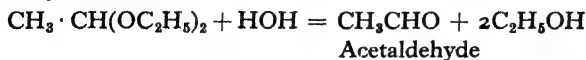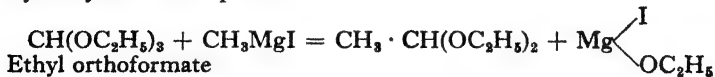
7. **Ethers:** by the action of a Grignard reagent of the type $R \cdot OMg \cdot X$ on an alkyl or aromatic halide:

$$C_2H_5O \cdot MgI + C_2H_5I = C_2H_5 \cdot O \cdot C_2H_5 + MgI_2$$
Ethyl ether

$$C_6H_5O \cdot MgBr + C_6H_5Br = C_6H_5 \cdot O \cdot C_6H_5 + MgBr_2$$
Phenyl ether
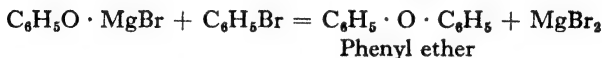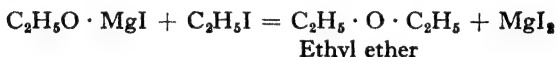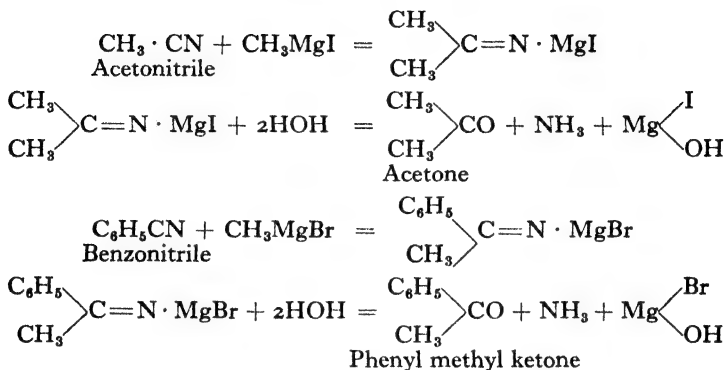
8. **Aldehydes:** by the action of a Grignard reagent on ethyl orthoformate, $CH(OC_2H_5)_3$, and subsequent hydrolysis of the product:

$$CH(OC_2H_5)_3 + CH_3MgI = CH_3 \cdot CH(OC_2H_5)_2 + Mg \diagup I$$
$$\diagdown OC_2H_5$$
Ethyl orthoformate

$$CH_3 \cdot CH(OC_2H_5)_2 + HOH = CH_3CHO + 2C_2H_5OH$$
Acetaldehyde

$$CH(OC_2H_5)_3 + C_6H_5MgBr = C_6H_5 \cdot CH(OC_2H_5)_2 + Mg \diagup Br$$
$$\diagdown OC_2H_5$$

$$C_6H_5 \cdot CH(OC_2H_5)_2 + HOH = C_6H_5 \cdot CHO + 2C_2H_5OH$$
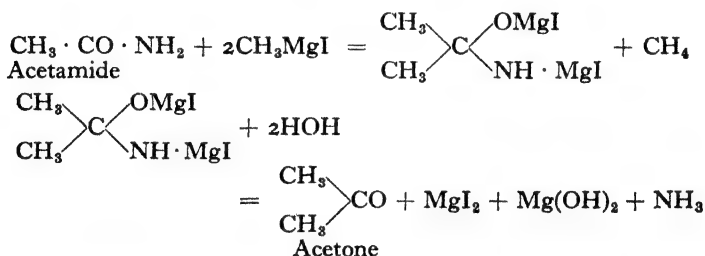Benzaldehyde
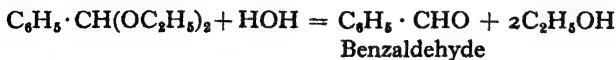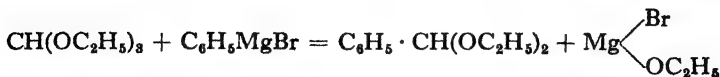
9. **Ketones:** by the action of a Grignard reagent on nitriles and amides, followed by hydrolysis of the additive compound produced:
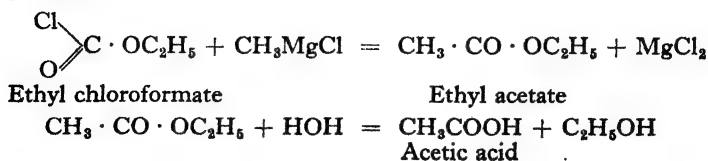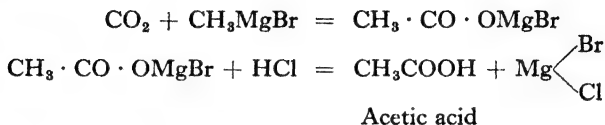
A. Nitriles

$$CH_3 \cdot CN + CH_3MgI = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!C\!=\!N \cdot MgI$$

Acetonitrile

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!C\!=\!N \cdot MgI + 2HOH = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!CO + NH_3 + Mg\!\!<\!\!\begin{matrix} I \\ OH \end{matrix}$$

Acetone

$$C_6H_5CN + CH_3MgBr = \begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!\!C\!=\!N \cdot MgBr$$

Benzonitrile

$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!\!C\!=\!N \cdot MgBr + 2HOH = \begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!\!CO + NH_3 + Mg\!\!<\!\!\begin{matrix} Br \\ OH \end{matrix}$$

Phenyl methyl ketone

B. Amides

$$CH_3 \cdot CO \cdot NH_2 + 2CH_3MgI = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} OMgI \\ NH \cdot MgI \end{matrix} + CH_4$$

Acetamide

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} OMgI \\ NH \cdot MgI \end{matrix} + 2HOH$$

$$= \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\!CO + MgI_2 + Mg(OH)_2 + NH_3$$

Acetone

10. **Acids.** (A) By the action of a Grignard reagent on ethyl chloroformate, followed by hydrolysis of the product:

$$\begin{matrix} Cl \\ O \end{matrix}\!\!>\!\!C \cdot OC_2H_5 + CH_3MgCl = CH_3 \cdot CO \cdot OC_2H_5 + MgCl_2$$

Ethyl chloroformate   Ethyl acetate

$$CH_3 \cdot CO \cdot OC_2H_5 + HOH = CH_3COOH + C_2H_5OH$$

Acetic acid   .
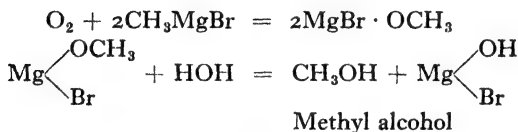
Benzoic acid is made similarly, using C_6H_5MgBr.

(B) By absorption of carbon dioxide by the appropriate Grignard reagent in ethereal solution. The gas is passed into the solution until it is saturated and the product is then treated with dilute acid:
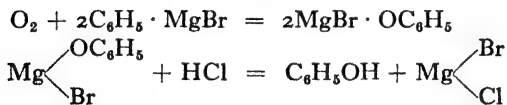
$$CO_2 + CH_3MgBr = CH_3 \cdot CO \cdot OMgBr$$

$$CH_3 \cdot CO \cdot OMgBr + HCl = CH_3COOH + Mg \langle {}^{Br}_{Cl}$$

Acetic acid

Benzoic acid is made similarly, using C_6H_5MgI or the corresponding bromine compound.

11. Alcohols and Phenols: by making a Grignard reagent absorb dry oxygen and treating the product with water or a mineral acid:

A. Alcohols

$$O_2 + 2CH_3MgBr = 2MgBr \cdot OCH_3$$

$$Mg \langle {}^{OCH_3}_{Br} + HOH = CH_3OH + Mg \langle {}^{OH}_{Br}$$

Methyl alcohol

B. Phenols

$$O_2 + 2C_6H_5 \cdot MgBr = 2MgBr \cdot OC_6H_5$$

$$Mg \langle {}^{OC_6H_5}_{Br} + HCl = C_6H_5OH + Mg \langle {}^{Br}_{Cl}$$

12. Conversions: A bromo-derivative can be converted into an iodo-derivative by first treating with dry magnesium powder and then adding iodine to the Grignard reagent produced:

$$C_6H_5 \cdot Br \xrightarrow{(Mg)} C_6H_5 \cdot MgBr \xrightarrow{(I_2)} C_6H_5I (+MgBrI)$$

QUESTIONS

1. What is a Grignard reagent?   How may it be prepared? What new substances may be obtained by a Grignard reagent from (*a*) methyl ethyl ketone, (*b*) acetaldehyde?

2. Explain how Grignard reagents may be used to synthesize (*a*) hydrocarbons, (*b*) alcohols, (*c*) acids, (*d*) ethers, (*e*) aldehydes, and (*f*) ketones.

3. Compare and contrast the reactions of (*a*) acetaldehyde and benzaldehyde, (*b*) ethyl alcohol and phenol, (*c*) ethyl iodide and iodobenzene.   (*B.Sc.*, *London*, *General*.)

PART II—PRACTICAL

Notes on Practical Work: Tests for Elements

Cleaning of Apparatus.—Before glass vessels are used it is essential that they should be clean and free from any grease. To ensure this, first rinse them out with a little concentrated nitric acid, taking care that no acid comes in contact with the fingers, then with sodium hydroxide solution, and finally with distilled water. Water should not adhere in drops to the wet surface of the glass. The inner surface of a burette can be cleaned if necessary with a little alcohol and ether on a small plug of cotton wool fastened to the end of a length of copper wire. After use all apparatus should be cleaned out thoroughly with distilled water before being put away.

A more efficient method of cleaning glass apparatus consists in the use of a saturated solution of potassium dichromate in concentrated sulphuric acid. The apparatus is filled with this solution and allowed to stand for five minutes; the solution is run out into a stock bottle and the apparatus is finally rinsed with much water. The dichromate solution can be used a considerable number of times. Use distilled water for making up solutions.

It is not essential to clean all glassware with sulphuric acid and dichromate solution after use, but all vessels should

be washed out, using a test-tube brush. If any vessel has been contaminated by oily or carbonaceous material during an experiment, it must be cleaned thoroughly.

Drying of Vessels.—In many tests and reactions in organic chemistry it is essential to have all vessels, e.g. beakers, flasks, condensers, perfectly dry. After the glassware is cleaned as already described, it should be left to drain in a rack; usually it will then be dry for use when required. A quicker method of drying apparatus is to wash first with distilled water and then with alcohol and finally to blow air through the warm vessel.

Instruments used for Measuring Liquids.—Graduated glass vessels are employed for measuring the volumes of liquids. Four different types are used: cylinders, flasks, pipettes and burettes. It is assumed that the student is familiar with the use of these instruments and with the methods used to calibrate them.

Unit of Capacity.

A litre is defined as the volume occupied by that quantity of pure water at 4° C. and normal atmospheric pressure, which has a mass of 1 Kgm. The unit of capacity in this case may be taken as one-thousandth of a litre, i.e. one millilitre (ml.).

The unit of capacity usually adopted is the cubic centimetre (c.c.), which is defined as the volume of a cube with a side of length 1 cm. A cubic centimetre of pure water at 4° C. does not weigh exactly 1 gm. In investigations of the standard litre in Paris in 1910 it was found that 1 litre of water at 4° C. occupies 1000·027 c.c. That is,

$$1 \text{ ml.} = 1\cdot000027 \text{ c.c.}$$

The difference between a millilitre and a cubic centimetre is so small that in ordinary volumetric work it may be dis-

regarded. Most graduated vessels are now calibrated in millilitres and in all calculations of the British Pharmacopœia the millilitre is employed.

Fire.—Many organic solvents are highly inflammable. Volatile liquids give off vapours which may explode on contact with hot surfaces. These substances include alcohol, ether, benzene, carbon disulphide, petroleum, acetone, toluene and glacial acetic acid. Hence when these are being used naked flames must be extinguished or removed to a considerable distance. Distillation of ether, acetone, carbon disulphide, petroleum, &c., should be conducted on the water bath, the latter being previously heated if possible, and the distilling flasks should be connected to a long condenser kept cool by running water. Failing this, any flame used must be protected by a wire gauze surrounding it, on the principle of the Davy safety lamp used by miners.

Recording of Results.

Notes should be written up at the time when the experiments are done.

Sentences should be written in the third person and in the past tense; e.g. do not write " I took a bottle and weighed it ", but " A bottle was taken and weighed ".

The notes should be arranged systematically, under the following headings:

1. *Experimental Problem.*

 e.g. (*a*) To identify the " unknown " substance given;
   (*b*) To examine the properties and reactions of urea.

2. *Method of Procedure*, which includes what is done and what happens. Diagrams of the apparatus employed (if any) should be given. In the case of " unknown " substance, arrange in three columns headed Test, Observation, Inference.

3. *Results*, in tabular form or otherwise. The results should be entered during the course of the experiment.

4. *Conclusions*, if any.

The account of an experiment should be so clear that anybody else reading it should have no difficulty in repeating the experiment exactly.

Tests for Elements in Organic Compounds

The elements which have to be tested for in organic compounds are carbon, hydrogen, halogens, nitrogen, sulphur, phosphorus, arsenic, and, in the case of metallic salts of organic acids, the metallic radicles.

Carbon and Hydrogen.—The organic nature of a compound is indicated by heating, when

(*a*) it may char, frequently swelling up and leaving a black residue;

(*b*) it may ignite and burn with a luminous smoky flame and deposit soot on a cold surface.

The black residue and soot can be proved to be carbon by the fact that they disappear completely on being heated to redness.

Detection of Organic Compounds.—Place a small quantity of naphthalene, just sufficient to cover a three-penny piece and no more, in the bottom of a crucible. Support this crucible on a pipe-clay triangle on a tripod. First heat the substance gently by placing a very small flame under the crucible and note the effect; increase the heating by raising the flame and finally heat to redness. Record all observations in a note-book.

Repeat the experiment, using the same amount of each of the following acids: oxalic, tartaric, citric, salicylic and benzoic.

Oxidation Tests: Carbon.—When the action of heat does not give any satisfactory result, place fine copper

oxide to the depth of $\frac{1}{4}$ in. in the bottom of a hard-glass test tube, then add a little of the substance—say, oxalic or benzoic acid—and mix intimately, using a glass rod. Then cover the mixture with a layer of coarse copper oxide about 1 in. deep. Fit the test tube with a cork and delivery tube bent at right angles, and place horizontally across a tripod so that the end of the delivery tube dips into lime water contained in a test tube. Heat the layer of coarse CuO first, then extend the heating to the mixture.

CO_2 is evolved, which turns the lime water milky.

Hydrogen.—In testing for hydrogen it is essential that all the materials should be dry. Cupric oxide is hygroscopic and must be thoroughly dried by heating in a crucible before use. Proceed as described under carbon. The hydrogen is detected either by the formation of moisture, which condenses in the delivery tube, or by placing a small amount of anhydrous copper sulphate in the front part of the test tube.

Halogens (Beilstein's Test).—Push one end of about 4 in. of stout copper wire into a cork. Heat the other end of the wire until it ceases to impart any colour to the flame. Allow to cool a little and dip into a small portion of the substance and heat again in the lower outer edge of the flame. A *green* flame generally indicates a **halogen,** but certain other substances, e.g. urea, give the test.

Use the following for practice: iodoform, chloral, and dibromocinnamic acid.

Nitrogen.—Grind the substance with about four times its bulk of dry soda lime and heat in a test tube:

(*a*) **Ammonia** evolved, test with moistened red litmus paper: indicates **nitrogen.**

(*b*) Grey sublimate, globules on rubbing: indicates **mercury.**

If the substance is soluble in water or dilute acids, apply inorganic tests for halides, sulphate, and phosphate.

Note.—The above test for nitrogen is only a simple positive test, since many compounds, e.g. nitro- and diazo-derivatives, do not give up their nitrogen in the form of ammonia.

Nitrogen, Sulphur, the Halogens (Lassaigne's Tests).—Place a pellet of clean sodium in the bottom of an ignition tube, then add an equal bulk of the substance. Heat the tube gently above the mixture, so as to melt the sodium. Remove the tube from the flame until any reaction ceases, and allow any distillate to run back on to the sodium, and reheat. When all action has ceased, heat the whole tube to redness until no more fumes are evolved. Plunge the red-hot tube into 25 c.c. of distilled water contained in a porcelain basin. If the tube is not completely immersed in the water and broken up, tap the tube cautiously with a pair of tongs. Boil the solution, and filter through a fluted filter. The filtrate should be quite clear, colourless and alkaline. Test this alkaline solution for

1. **Sulphur.**—To about 1 c.c. add a drop of lead acetate solution: *brown* or *black* precipitate indicates **sulphur.**

2. **Nitrogen.**—To about 2 c.c. add one or two crystals of ferrous sulphate, boil well and acidify with concentrated hydrochloric acid; filter through a fluted filter: *blue* precipitate on filter indicates **nitrogen.**

If no nitrogen is present, only a yellow solution will be obtained. If the solution is green with no blue precipitate, allow to stand, or repeat ignition with sodium, taking care that the substance actually comes in contact with the melted sodium and is well heated.

If sulphur is present, a black precipitate soluble in HCl is formed with ferrous sulphate.

3. **Bromine, Iodine.**—Take 5 c.c. and acidify with sulphuric acid. (If N and S are present, however, add an equal volume of dilute sulphuric acid, dilute to about 30 c.c. with water, boil vigorously in a porcelain dish for

10 minutes and cool.) Then add chlorine water; if a yellow or brown solution results, shake well with about 2 c.c. of carbon disulphide.

> CS$_2$ coloured *brown*: **bromine.**
> CS$_2$ coloured *violet*: **iodine.**

4. **Chlorine.**—Take 10 c.c. and acidify with dilute nitric acid. (If N, S, Br, or I are present add twice the volume of dilute HNO$_3$, boil vigorously in a porcelain dish for 10 minutes and cool.) Add silver nitrate solution: a white curdy precipitate indicates **chlorine.**

For practice:

Test Sulphanilic acid for N and S.

  ,,   Iodoform for iodine.

  ,,   Chloramine-T for N, S and Cl.

  ,,   Aniline hydrochloride for N and Cl.

  ,,   Dibromocinnamic acid for Br.

Phosphorus and **Arsenic.**—Place as much of a mixture of K$_2$CO$_3$ and KNO$_3$ as will cover a sixpence in the bottom of a crucible. Fuse this mixture and add small quantities of the substance at a time, waiting in each case until all action has ceased before adding more. Heat until all carbon has burnt away. Allow to cool, acidify with dilute nitric acid, warm with ammonium molybdate solution: yellow precipitate indicates **phosphorus** or **arsenic.** Test for arsenic by inorganic methods.

For practice: Test triphenyl phosphate for phosphorus.

Metallic Radicles.—Metals are detected in organic compounds as follows. A small quantity of the substance is placed in a crucible and just moistened with 50 per cent sulphuric acid, using a dropping tube. The crucible is placed on a pipe-clay triangle on a tripod and heated with a small flame until dry. If the dry charred mass has swollen up, press it down into the bottom of the crucible with a glass rod. Heat to redness until all the carbon has

burnt away. A residue will be the sulphate or oxide of the metal.

To detect the metal, the residue is dissolved in water or in dilute HCl, and is then dealt with as in Inorganic Analysis. If the residue is insoluble either in water or in dilute HCl, ignite the organic substance by itself, boil with dilute HCl and filter.

For practice use cream of tartar, lead benzoate, zinc acetate, &c.

Determination of the Melting-point.

In view of the fact that numerous organic substances have a definite melting-point by which the compound may be identified, the student should now proceed to determine the melting-points of one or two of the following substances: Iodoform, salicylic acid, cinnamic acid, stearic acid, benzoic acid.

Fig. 41.—Melting-point Apparatus

Powder the substance finely and press it between filter papers. If the substance feels damp, dry it in a desiccator or in a steam oven (provided the organic substance does not decompose at 100° C.). A capillary tube should now be made by heating a piece of glass tubing in a flame and drawing it out when soft to a length

of about two feet and bore of 1 mm. Cut off lengths of 3 in. and seal one end. Now scoop up a little of the substance with the open end of the capillary and tap the closed end on the bench so as to shake it down to the bottom of the tube. The substance when closely packed should only be about $\frac{1}{8}$ in. deep. Attach this capillary to a thermometer by a rubber ring cut from the end of a piece of rubber tubing, so that the ring is near the top of the capillary and the substance opposite the middle of the thermometer bulb.

Support a boiling tube in a clamp. Fit the tube with a cork bored to take the thermometer and cut a groove vertically in the side of the cork so that the scale of the thermometer can be read. Remove the cork and pour concentrated sulphuric acid into the dry tube so that when the end of the thermometer is about half an inch from the bottom of the tube the acid is about $\frac{1}{4}$ in. above the bulb of the thermometer (fig. 41). On no account let the acid touch the rubber ring. Now take a rough melting-point of the substance, raising the temperature fairly rapidly and noting the temperature at which the solid changes to a liquid. Move the flame to and fro when heating the boiling tube. Repeat with a fresh capillary tube, raising the temperature rapidly to within 10–15° of the melting-point, and then heat very gradually, using a very small flame, so that the temperature rises about 2° per minute. Remove the flame from time to time

Fig. 42.—Melting-point Flask

as the temperature approaches the melting-point. If the acid darkens add one or two crystals of potassium nitrate.

To avoid the risk of the sulphuric acid coming into contact with the rubber ring and destroying it (which would cause the acid to blacken) the determination of the melting-point of a substance may be conducted in a small flask of
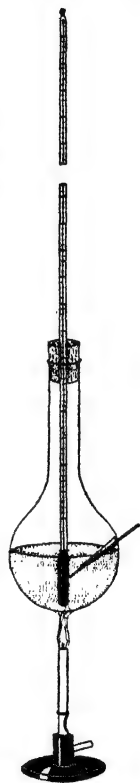
capacity from 50 to 100 c.c., with a tapering tube either blown or sealed into its side as shown in fig. 42. The small capillary tube used to determine the melting-point is inserted through the aperture of this tube so that the closed end just touches the bulb of the thermometer immersed in sulphuric acid or paraffin.

This apparatus has an advantage over the boiling tube method in that the thermometer remains permanently fixed and the capillary tube is easily removed after the experiment, and so there is no danger of the acid coming into contact with the skin. In order to ensure complete accuracy the apparatus may be modified by having two inlet tubes sealed into the flask at opposite sides in order to insert two capillary tubes containing the substance. The mean of two melting-point readings may then be taken as the true melting-point.

QUESTIONS

1. Carefully describe the more important tests by which you would show the presence of carbon, hydrogen, nitrogen and sulphur in an organic substance.

2. By what tests would you recognize the presence of each of the following elements in a carbon compound: Calcium, chlorine, phosphorus, bromine?
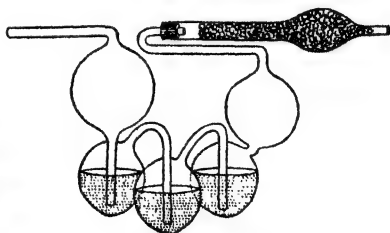
CHAPTER XXI

Quantitative Analysis

A qualitative analysis of an organic compound by the methods just outlined must be followed by a quantitative analysis to determine the percentages of the various elements present.

Carbon and Hydrogen

The determination of carbon and hydrogen is carried out in one operation. The principle of this method is that all organic compounds are decomposed when brought into contact with red-hot copper oxide, the carbon being converted into carbon dioxide and the hydrogen into water. The carbon dioxide is absorbed in potash bulbs
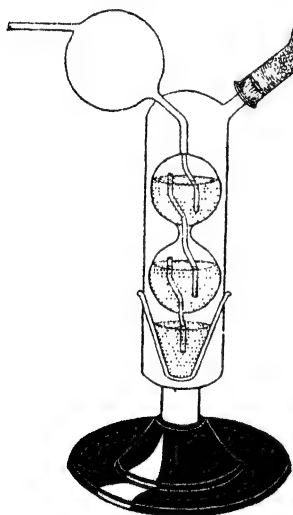
Bender's Potash Bulb   Mohr's Potash Bulb

Fig. 43

(fig. 43) and the water in calcium chloride tubes (fig. 44).

Liebig's Method (1831).—The organic substance whose determination is to be found undergoes combustion in a combustion furnace.

The combustion tube (fig. 45) consists of a piece of hard glass tubing or preferably silica tubing, about 1 cm. in internal diameter and 90 cm. long, open at both ends. A weighed amount (about 0·15 to 0·2 gm.) of the organic substance is introduced in a narrow porcelain or platinum boat B. More than half the length of the tube is packed with copper oxide wire kept in position by asbestos plugs P or small spirals of oxidized copper gauze. A spiral of copper gauze or platinum foil is placed at A to prevent backward diffusion of the products of combustion. If a volatile liquid is to be analysed it is weighed in a thin glass bulb or in a Victor Meyer's bottle and placed in the boat. The combustion tube is then placed in a combustion furnace (fig. 46). The end D (fig. 45) is connected to a weighed calcium chloride tube E, and the latter to a weighed set of potash bulbs F, half filled with a

Fig. 44.—Calcium Chloride Tube

Fig. 45.—Combustion Tube for the Estimation of Carbon and Hydrogen

C   A   B P   CuO   P G   D

40 per cent solution of potassium hydroxide. The other end C is connected to a supply of air or oxygen. This may be conveniently obtained from a reservoir, the gas being driven out by the entry of a slow stream of water. The gas is passed over soda lime or through strong caustic potash
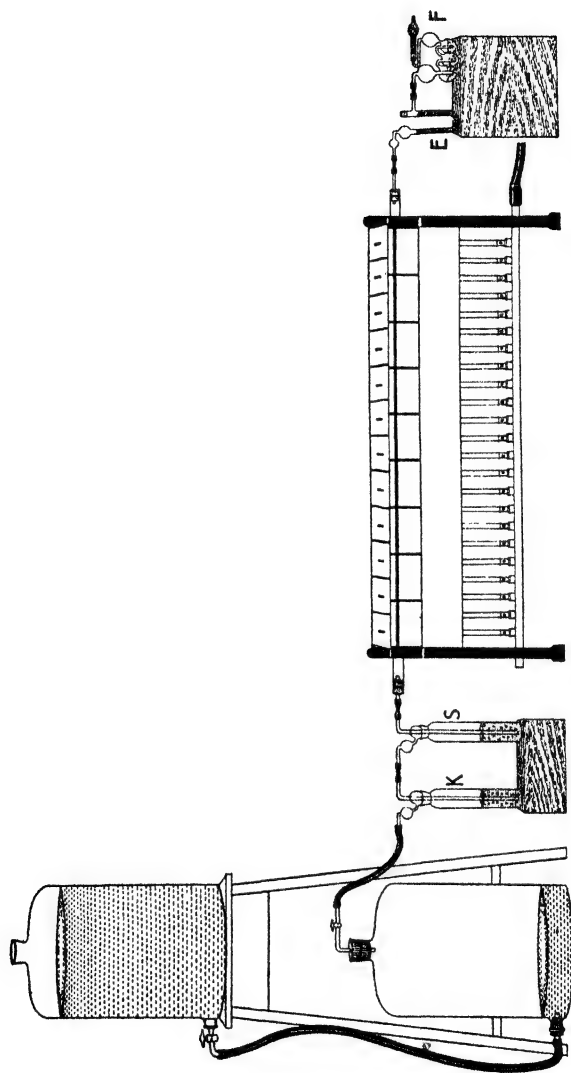
Fig. 46.—Combustion Furnace for determining Carbon and Hydrogen in an Organic Compound

solution (K) to free it from carbon dioxide and through concentrated sulphuric acid (S) contained in a Drechsel bottle to free it from moisture. The calcium chloride tube and potash bulbs are not connected until all moisture and carbon dioxide have been driven out and the copper oxide and gauze are completely oxidized. To ensure this the furnace is lit half an hour previously to heat the combustion tube. The organic substance is then admitted, the apparatus is connected up and the air allowed to pass for about 2 to 3 hours at the rate of two to three bubbles a second. The calcium chloride tube and potash bulbs are weighed after the experiment and the amounts of carbon and hydrogen present are calculated as follows:

Hydrogen from the gain in weight of the calcium chloride tube. This weight is the weight of water formed; one-ninth of this increase is the weight of hydrogen:

$$2H_2 + O_2 = 2H_2O$$
$$4 \text{ gm. } H_2 \equiv 36 \text{ gm. } H_2O$$
i.e. $\qquad 1 \text{ gm. } H_2 \equiv 9 \text{ gm. } H_2O.$
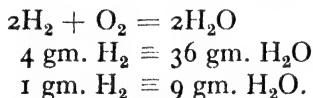
Carbon from the gain in weight of the potash bulbs. This weight is the weight of carbon dioxide formed. Three-elevenths of this increase is the weight of carbon:

$$C + O_2 = CO_2$$
$$12 \text{ gm. } C \equiv 44 \text{ gm. } CO_2$$
i.e. $\qquad 3 \text{ gm. } C \equiv 11 \text{ gm. } CO_2.$
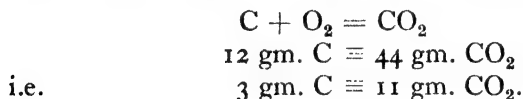
Example.

Weight of cane sugar taken   = 0·228 gm.
Weight of calcium chloride tube
    and water   = 34·870 ,,
Weight of calcium chloride tube = 34·738 ,,
Weight of water   = 0·132 ,,

$$\text{Percentage of } \textit{hydrogen} = \frac{1}{9} \times \frac{0·132}{0·228} \times \frac{100}{1}$$
$$= 6·43$$

Weight of potash bulbs and $CO_2 = 58\cdot284$ gm.

Weight of potash bulbs $\qquad = 57\cdot932$,,

Weight of CO_2 $\qquad = 0\cdot352$,,

Percentage of *carbon* $\quad = \dfrac{3}{11} \times \dfrac{0\cdot352}{0\cdot228} \times \dfrac{100}{1}$

$\qquad\qquad\qquad\qquad = 42\cdot11$

The remainder, namely $51\cdot46$ per cent, is *oxygen*.

For practice: Estimate the percentages of carbon and hydrogen in (*a*) oxalic acid, (*b*) benzoic acid, (*c*) toluene, (*d*) cane sugar.

Modifications in the combustion tube are required when:

(*a*) *Nitrogen* is present. A bright spiral of copper gauze about 2 in. long is placed in the tube at G (fig. 45). This spiral must be kept red-hot to reduce the oxides of nitrogen formed to nitrogen, which is not absorbed by the potash bulbs.

(*b*) *Sulphur, halogen,* or *phosphorus* is present. About half of the copper oxide is replaced by fused lead chromate, in order to convert any chlorine, sulphur dioxide, &c., formed into lead chloride, lead sulphate, &c., and thus prevent them from passing into the absorption apparatus.

For practice: Estimate the carbon and hydrogen present in (*a*) thio-urea, (*b*) sulphanilic acid.

Nitrogen

This element is estimated by:

1. The combustion method of (*a*) Dumas, (*b*) Will and Varrentrap.

2. The ammonia method of Kjeldahl.

Dumas' Method.—The principle of this method is that most nitrogenous organic compounds when heated with copper oxide in an atmosphere of carbon dioxide

liberate nitrogen in the free state, in which it can be collected and measured.

A known weight of substance (about 0·2 gm.) is mixed with copper oxide and placed in a tube as in Liebig's method. The tube is packed as shown in fig. 47. The function of the copper spiral is to decompose any oxides of nitrogen which may be formed in the combustion: if these were allowed to pass over unchanged they would be absorbed in the caustic potash and the measured volume of nitrogen would be too small. The combustion tube is placed in the combustion furnace and a steady stream of carbon dioxide is passed over. This carbon dioxide is generated in a tube filled with sodium bicarbonate, which is gently heated. It is essential that carbon dioxide should be passed through the tube to displace the air before heating commences. When all the air is expelled from the tube the open end is joined to a graduated tube or Schiff's nitrometer filled with 40 per cent caustic potash solution. The bottom of the nitrometer contains mercury, which serves as a " trap ", allowing the entry of gas from the combustion tube but preventing the flow of caustic potash back. The stream of carbon dioxide is then slowed down; all the gas which collects in the nitrometer is absorbed, and any air which has collected is allowed to escape by raising the reservoir and opening the tap. The combustion is now proceeded with; the burners under the copper spiral and the layers of coarse copper oxide at both ends are slowly turned on, and later the fine copper oxide layers and mixture are heated. When gas is no longer evolved the stream of carbon dioxide is again allowed to flow so as to sweep out all traces of nitrogen. The apparatus is then allowed to cool, the levels are adjusted, and the volume of gas is read off, and corrected to S.T.P.

The Dumas method usually gives a result too high by about 0·3 per cent, owing, no doubt, to the impossibility of drawing out all the air. Instead of using bicarbonate of soda to generate carbon dioxide, this gas may be obtained
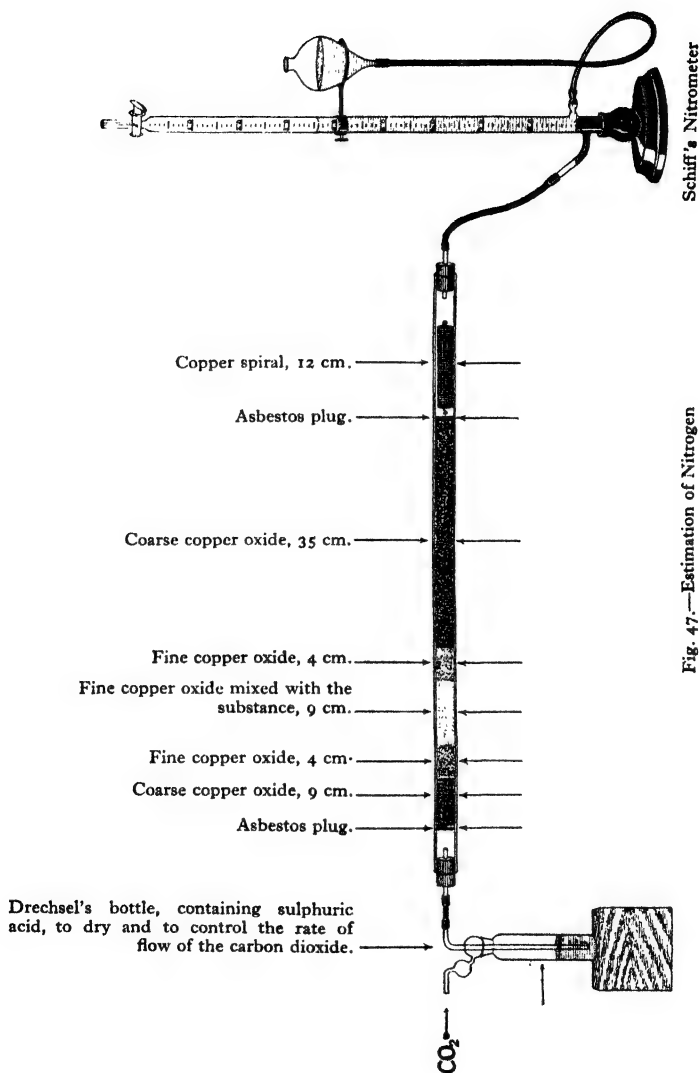
Copper spiral, 12 cm.

Asbestos plug.

Coarse copper oxide, 35 cm.

Fine copper oxide, 4 cm.

Fine copper oxide mixed with the substance, 9 cm.

Fine copper oxide, 4 cm·

Coarse copper oxide, 9 cm.

Asbestos plug.

Drechsel's bottle, containing sulphuric acid, to dry and to control the rate of flow of the carbon dioxide.

CO_2

Schiff's Nitrometer

Fig. 47.—Estimation of Nitrogen

from a cylinder or Kipp's apparatus, care being taken to see that no air is mixed with the gas.

Example.

Weight of organic substance = 0·2248 gm.
Volume of nitrogen collected = 7·1 c.c.
    Temperature of gas   = 16° C.
    Pressure of air   = 75·36 cm.
    Vapour pressure   = 13·6 mm. (9·62 mm. for KOH).

Volume of gas corrected to S.T.P. = $7·1 \times \dfrac{273}{289} \times \dfrac{740}{760}$ c.c.

Since 1 c.c. of nitrogen at S.T.P. weighs 0·001251 gm.,

Weight of nitrogen collected = $7·1 \times \dfrac{273}{289} \times \dfrac{740}{760} \times 0·001251$

$$= 0·00817 \text{ gm.}$$

Percentage of nitrogen = $\dfrac{0·00817}{0·2248} \times 100 = 3·63$

For practice: Estimate the percentage of nitrogen in (*a*) nitraniline (use about 0·20 gm.), (*b*) quinine (use about 0·30 gm.).

Calculate the results from the formula:

Percentage of nitrogen

$$= V \times \frac{273}{(273 + t)} \times \frac{(P - p)}{760} \times \frac{0·001251}{W} \times 100,$$

where

    V = observed volume of nitrogen,
    W = weight of organic substance taken,
    P = barometric pressure in mm.,
    p = vapour pressure of potash solution, roughly equal
        to that of water (see Appendix I),
    t = temperature of potash solution.

Will and Varrentrap's Method.—The principle of this method is that most nitrogenous organic substances when heated with soda lime yield their nitrogen in the form of ammonia. The ammonia evolved from a known weight of the substance is absorbed in a known excess of standard acid. The excess of acid is estimated by back titration with a standard alkali.

This method is not applicable to compounds in which nitrogen is directly linked to oxygen, e.g. nitro-, nitroso-, and azoxy-compounds.

The apparatus consists of a piece of hard glass tube about 50 cm. long, drawn out and sealed at one end and packed as shown in fig. 48. The absorption apparatus A contains standard hydrochloric acid to absorb the ammonia. The combustion tube is heated in the furnace, commencing at B, and is gradually raised to a red heat; the ammonia remaining in the tube is drawn

Absorption apparatus containing standard HCl. ——▶ A

Asbestos plug, 1·5 cm. ——▶ B

Coarse soda lime, 25 cm. ——▶

Mixture of fine soda lime and substance, 9 cm. ——▶

Coarse soda lime, 4·5 cm. ——▶

Asbestos plug, 1·5 cm. ——▶

S
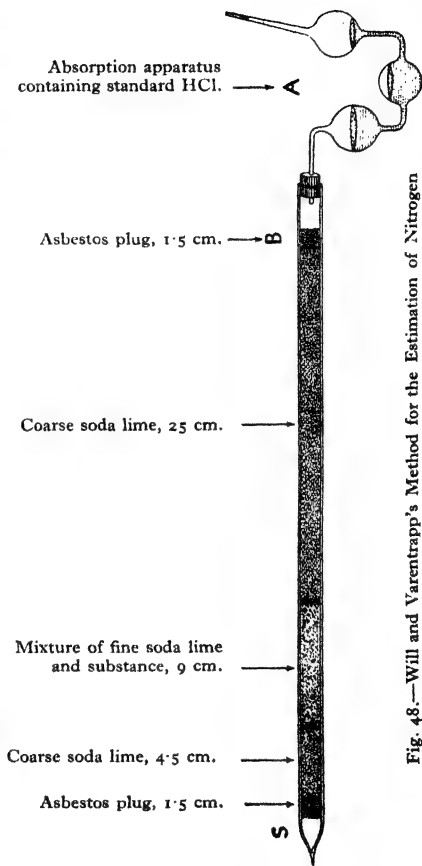
Fig. 48.—Will and Varrentrapp's Method for the Estimation of Nitrogen

through the absorption apparatus by breaking the seal S and aspirating air through the tube.

$$HCl \equiv NH_3 \equiv N$$

1000 c.c. $N \cdot HCl \equiv 14$ gm. of nitrogen

$\therefore$ 1 c.c. $N \cdot HCl \equiv 0 \cdot 014$ gm. nitrogen

or   1 c.c. $N/10 \; HCl \equiv 0 \cdot 0014$ gm. of nitrogen

This method is not often used, as the results are too low, owing to decomposition of the ammonia.

For Practice: Estimate the percentage of nitrogen in (a) acetanilide (use 0·3 gm.), (b) quinine, and (c) carbazole.

Kjeldahl's Method.—The principle of this method of estimating nitrogen is that most nitrogenous organic bodies when boiled with concentrated sulphuric acid, or a mixture of this acid and potassium sulphate, are completely oxidized, the nitrogen being converted into ammonia, which combines with the sulphuric acid to form ammonium sulphate.

The ammonia is then estimated volumetrically by distilling the sulphate with excess of sodium hydroxide and collecting the gas in standard acid.

This method gives good results with the following groups of organic compounds: amines, ammonium compounds, alkaloids, proteins, and their related compounds. It is the usual method for the estimation of nitrogen in feeding-stuffs, animal fluids, organized tissues, nitrogenous foods, e.g. milk, bread, cheese, and all excretions, e.g. urine.

The Kjeldahl method, however, is not applicable to all organic compounds, and usually fails when the nitrogen is linked directly to any element other than carbon or hydrogen, as in nitro-, nitroso-, azo-, azoxy-, hydrazo-, and diazonium compounds, and probably in cyanogen derivatives and platinichlorides of bases. Moreover, cyclic nitrogen compounds, such as pyridine and quinoline, cannot be estimated by the Kjeldahl method.

Procedure.—Weigh out accurately o·1 to 3 gm. of the substance, according to the anticipated content of nitrogen, into a Kjeldahl flask made of Jena or resistance glass and of capacity 300 c.c. (fig. 49). The flask is pear-shaped, with a long neck which can be closed by a loosely fitting glass bulb to condense some of the vapours which escape by condensation. Then add about 12 gm. of pure anhydrous potassium sulphate and about 30 c.c. of pure concentrated sulphuric acid. Finally add a small crystal of copper sulphate or a small globule of mercury.

The object of adding (*a*) the potassium salt, is to promote oxidation by raising the boiling-point of the liquid; (*b*) the copper sulphate or mercury, is to assist oxidation by catalysis. The mercury is eventually converted to mercuric sulphate, which acts as the true catalyst.

The flask is clamped over wire gauze in a

Fig. 49.—Kjeldahl Flask

slightly inclined position and gently boiled. The contents first become almost black; boiling is continued until the solution becomes colourless or faintly yellow, or the colour of dilute copper sulphate. The duration of boiling depends on the substance. In some cases boiling for half an hour is sufficient, whereas in others six to ten hours will be required. As sulphur dioxide is evolved in large quantities, the operation should be conducted in a fume cupboard.
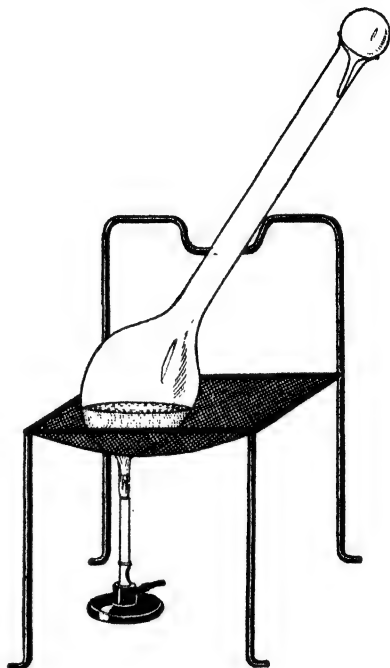
The flask is then allowed to cool and the contents are poured into 100 c.c. of cold water contained in a round-bottomed flask (A) (fig. 50) of capacity about 1 litre; the Kjeldahl flask is rinsed out four times with about 30–40 c.c. of water each time, the rinsings being transferred to flask A, which is cooled under the tap.
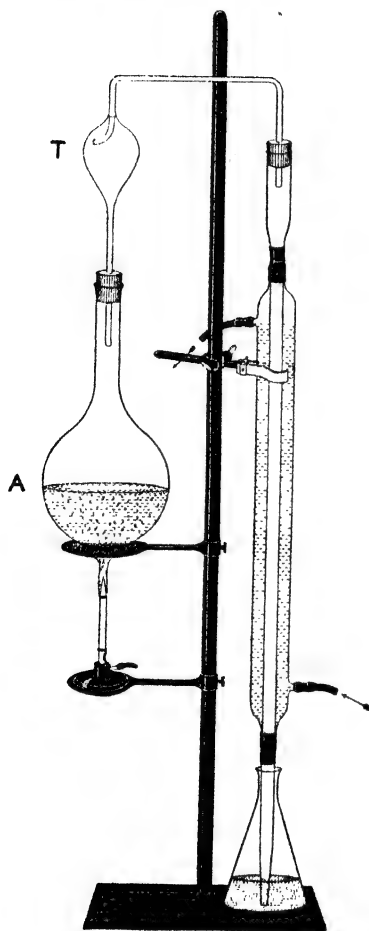

Fig. 50.—Estimation of Nitrogen by Kjeldahl's Method

Forty grammes of sodium hydroxide in 100 c.c. of water are then carefully poured down the side of this flask so that the alkali forms a layer below the acid. The amount of sodium hydroxide taken must be in sufficient excess to neutralize the acid and to render the solution strongly alkaline. A few pieces of porous pot or granulated zinc are then introduced to prevent bumping. (Zinc is attacked by the alkali and the bubbles of hydrogen evolved tend to prevent overheating.)

The flask A, fitted with a rubber cork through which is inserted a bulb adapter or trap T, is then connected with an upright condenser.

The end of the condenser just dips below the surface of 100 c.c. of N/10 hydrochloric or sulphuric acid con-

tained in a small flask. The apparatus must be tested for leakage.

The object of the trap is to prevent any alkali being carried over into the receiver.

The flask is now shaken to mix the contents and the liquid is boiled briskly to drive off the liberated ammonia, which is absorbed in the standard acid. The distillation should continue for at least half an hour, or until no more ammonia is evolved. This should be ascertained by testing a drop of the distillate with red litmus paper. When the operation is complete the condenser is washed out into the receiver with distilled water.

The amount of acid which has been neutralized by the ammonia is then estimated by back titration with $N/10$ sodium hydroxide, using methyl orange as indicator.

$$1 \text{ c.c. } N/10 \text{ acid} = 0.0017 \text{ gm. of ammonia}$$
$$= 0.0014 \text{ gm. of nitrogen.}$$

Example.—0.6837 gm. of acetanilide treated by Kjeldahl's method liberated ammonia which was passed into 100 c.c. of $N/10$ sulphuric acid. The excess of acid required 49.1 c.c. $N/10$ sodium hydroxide for neutralization.

Amount of acid used $= 100 - 49.1$ c.c. $= 50.9$ c.c.
Amount of nitrogen present $= 50.9 \times 0.0014$ gm.

$\therefore$ Percentage of nitrogen present in acetanilide
$$= \frac{50.9 \times 0.0014 \times 100}{0.6837}$$
$$= 10.42.$$
Theoretical percentage $= 10.37$.

In most cases the result obtained is too high. This error is due to alkali being washed out of the glass of the condenser by the condensing steam. For this reason it is advisable to use a hard glass condenser tube, or one made of block tin.

Notes.—1. Care must be taken to ensure that excess of standard acid is present. It is therefore advisable to add a drop of methyl orange to the acid before the distillation is commenced. If the colour changes additional acid must be added immediately, before any appreciable amount of ammonia has been lost.

2. If mercuric sulphate or mercury is used as a catalyst, sodium sulphide in small quantity must be added to the ammonium salt to decompose any ammoniacal mercury compounds which may be formed.

For practice: Use the following quantities for the estimation of nitrogen by the Kjeldahl method in the substances stated below:

Acetanilide	$C_6H_5 \cdot NH \cdot CO \cdot CH_3$	0·6 to 0·7 gm.
Uric acid	$C_5H_4N_4O_3$	0·2 to 0·3 gm.
Glycine	CH_2NH_2COOH	0·3 to 0·4 gm.
Hippuric acid	$(C_6H_5CO) \cdot NH \cdot CH_2COOH$	1·0 gm.
Cheese		1·0 gm.
Bread		5·0 gm.
Milk or urine		10 c.c.

The Nitrometer

The nitrometer is so called because it was devised originally for the analysis of " nitrous vitriol ". It is used in certain analytical processes which involve the measurement of a gas. Schiff's nitrometer is illustrated on p. 503 (fig. 47).

The Lunge nitrometer as modified by Allen (fig. 51a) is the type most frequently used. It consists of a graduated measuring tube A, of capacity 50 c.c., fitted with a three-way stopcock B communicating with a small cup C and a capillary outlet tube D to which a flask F may be fitted for the external generation of a gas. In most cases, however, the gas is generated in the nitrometer itself. The graduated tube is connected by means of thick-walled rubber tubing with the pressure tube E.

The apparatus is usually charged with mercury, although

strong brine, water, glycerine, or oil may be used for special purposes instead of mercury.

The working of the three-way stopcock is self-explanatory; a gas can be drawn into the graduated tube through D, or a liquid from the cup C.
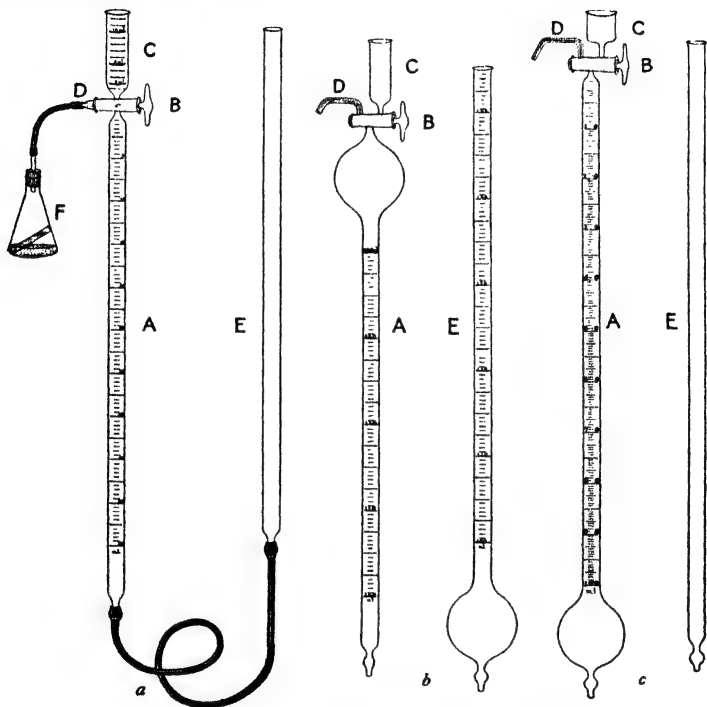

Fig. 51.—Nitrometers

a, Lunge's, modified by Allen; b, Lunge's; c, Tennant's

The student should practise the admission and ejection of gases and liquids before employing the nitrometer for quantitative estimations.

Other forms of nitrometers include:

(1) The ordinary Lunge nitrometer (fig. 51b), for measuring larger volumes of gas. This form has a bulb blown in

the measuring tube immediately below the stopcock. This bulb has a capacity of nearly 100 c.c., and the first graduation on the tube below the bulb is for 100 c.c.; the graduations are continued down the tube to 140 c.c. A bulb of the same capacity must also be blown on the lower part of the pressure tube to hold the mercury or other liquid.

(2) The Tennant nitrometer (fig. 51c). This has a three-way stopcock and a bulb at the bottom of the graduated tube.

The following substances can be estimated by the nitrometer.

Nitric Acid (Nitrous Vitriol).—Charge the apparatus with mercury by pouring the mercury into the pressure tube until it is two-thirds full. Then raise the pressure tube until the mercury just enters the stopcock. Remove all air bubbles adhering to the inside of the tube. Lower the tube E and pour into the cup a known quantity of nitrous vitriol freed from SO_2 by the addition of a little powdered potassium permanganate. About 0·5 to 5 c.c. of acid are used according to the quantity of nitric oxide which it is believed to contain.

The nitrous vitriol is cautiously admitted into the measuring tube by opening the stopcock. 3 c.c. of concentrated sulphuric acid are then allowed to run into the measuring tube, followed by a further 3 c.c., care being taken that no air enters the tube. The cup is rinsed out with water, which is withdrawn by means of a pipette and rejected. This is done to prevent any corrosive action on the skin when the tube is shaken.

The graduated tube is held by the cup and the bottom and lowered almost to a horizontal position so that the substances interact and nitric oxide is evolved. Repeat several times, and finally shake up the mercury with the acid until no more gas is evolved. Use a rotary movement to produce an intimate mixture of the acid with small globules of mercury.

Clamp the graduated tube in an upright position and adjust the mercury levels, allowing 1 mm. of mercury in

the pressure tube above the mercury level in the graduated tube for every 7·6 mm. of the concentrated acid.

Allow the apparatus to stand for half an hour and read the volume of gas evolved when the temperature assumes that of the air, or cool the tube with running water. Note the temperature and pressure and adjust the volume accordingly.

The reaction is as follows:

$$2HNO_3 + 3H_2SO_4 + 6Hg = 2NO + 3Hg_2SO_4 + 4H_2O,$$

whence

1 c.c. of NO at S.T.P. $\equiv$ 0·00134 gm. of nitric oxide
$\equiv$ 0·000626 gm. of nitrogen
$\equiv$ 0·001698 gm. of nitrogen trioxide
$\equiv$ 0·002814 gm. of nitric acid
$\equiv$ 0·00451 gm. of KNO_3.

The gas and acid are then ejected into a beaker. This is done by raising the pressure tube until the mercury begins to flow out through the capillary tube.

Urea.—Urea in urine is estimated by the action of a solution of sodium hypobromite on the liquid.

Sodium hypobromite is prepared by dissolving 40 gm. of sodium hydroxide in 100 c.c. of water and adding 10 c.c. of bromine.

$$2NaOH + Br_2 = NaBr + NaOBr + H_2O.$$

Procedure.—Pour into the decomposition flask F (fig. 51a) 25 c.c. of the hypobromite solution and suspend by means of a piece of cotton a small test tube containing 5 c.c. of urine so that the tube just touches the bottom of the flask and is in an inclined position. A cork containing a short delivery tube is inserted into the neck of the flask in such a way that the tube is kept in position. This delivery tube is connected by a short piece of rubber tubing to the graduated vessel A, which is filled with water or mercury by

raising the reservoir E. In order to ensure that the flask is under atmospheric pressure, the three-way tap B is turned so that the air in the flask is momentarily in contact with the outer air. The tap B is turned to connect the flask F directly with A; when this has been done, the flask is tilted so that the urine is poured on to the hypobromite solution. Nitrogen is evolved and the liquid in A is depressed. When the reaction has ceased the flask is allowed to cool (20 minutes) to room temperature, the levels of the liquids in A and E are adjusted, and the volume of nitrogen is noted. This volume is then corrected for atmospheric temperature, pressure, and tension of water vapour in the usual way.

$$CO(NH_2)_2 + 3NaOBr = 3NaBr + N_2 + CO_2 + 2H_2O;$$

60 gm. of urea $\equiv$ 22·4 litres of nitrogen at S.T.P.

$\therefore$ 1 c.c. $N_2 \equiv$ 0·0026786 gm. of urea

$\equiv$ 0·002952 gm. of urea (corrected for loss).

Notes.—1. The volume of nitrogen evolved from urea by this method is only 92 per cent of the theoretical amount, and a correction must be made, as indicated above.

2. The carbon dioxide evolved is absorbed by the excess of alkali present in the hypobromite solution.

3. Other nitrogenous bodies in the urine also yield a small volume of nitrogen, but so small that it may be disregarded.

4. In cases of diabetes the urine contains glucose, which increases the volume of nitrogen evolved. In order to estimate the actual volume of nitrogen evolved from urea in diabetic urine, cane sugar is added to the extent of ten times the weight of urea contained in the sample of urine under examination. (A rough estimate of the urea present is first made, using 5 c.c. of urine. The requisite amount of cane sugar is added to a further 5 c.c. of urine and an accurate determination made as already described).

Purity of Urea and of Ammonium Salts.—The

purity of urea may be determined by weighing out 1 gm. and dissolving in water made up to 100 c.c. Introduce 5 c.c. of this solution into the small tube in the decomposition flask containing 25 c.c. of sodium hypobromite and proceed as above.

In the case of ammonium salts weigh out 0·25 gm. of the solid and proceed as above.

$$2NH_3 + 3NaOBr = 3H_2O + N_2 + 3NaBr,$$
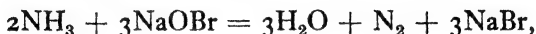
whence 1 c.c. of nitrogen

        ≡ 0·001518 gm. of ammonia

        ≡ 0·004777 gm. of ammonium chloride

        ≡ 0·005893 gm. of ammonium sulphate.

In order to ensure that all the nitrogen is evolved, excess of cane sugar must be added.

Substances which Evolve Carbon Dioxide.—The following substances may be estimated by using the decomposition flask and tipping tube:

    Carbonates and bicarbonates;
    Limestone, calcspar, and bone charcoal;
    Oxalates by manganese dioxide;
    Manganese in manganese ores by oxalic acid.

Owing to the solubility of carbon dioxide in the acid solution used, an addition of 7 per cent must be added to the observed volume, if 10 c.c. of hydrochloric acid of specific gravity 1·12 are used for the decomposition of the carbonate.

Use about 0·2 to 0·25 gm. of the substance:

1 c.c. of carbon dioxide at S.T.P.

        ≡ 0·004732 gm. of Na_2CO_3

        ≡ 0·004464 gm. of $CaCO_3$.

        ≡ 0·00194 gm. of MnO_2

        ≡ 0·00201 gm. of $(COOH)_2$.

Nitrites and Nitrates.—The substance is weighed out and dissolved in 1 to 2 c.c. of water. In this case the apparatus is charged with mercury. The solution is placed in the cup and introduced into the measuring tube, care being taken not to admit any air. The cup is then washed with about 1 c.c. of water, which is drawn into the tube. Concentrated sulphuric acid (3 c.c.) is then admitted and the mixture shaken violently with the mercury. The volume of nitric oxide is read off after half an hour.

$$2KNO_3 + 6Hg + 4H_2SO_4$$
$$= 2NO + K_2SO_4 + 3Hg_2SO_4 + 4H_2O.$$
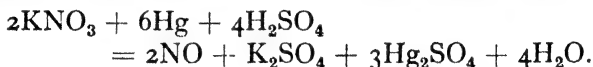
101 gm. $KNO_3 \equiv$ 22·4 litres of nitric oxide at S.T.P., whence

$$1 \text{ c.c. NO} \equiv 0·004516 \text{ gm. of } KNO_3$$
$$\equiv 0·003794 \text{ gm. of } NaNO_3.$$

The reaction for nitrites is as follows:

$$2NaNO_2 + 2Hg + 2H_2SO_4$$
$$= 2NO + Na_2SO_4 + Hg_2SO_4 + 2H_2O.$$
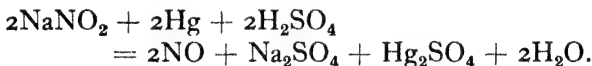
69 gm. $NaNO_2 \equiv$ 22·4 litres of nitric oxide at S.T.P., whence

$$1 \text{ c.c. NO} \equiv 0·00308 \text{ gm. of } NaNO_2.$$

Note.—For the smaller nitrometer use about 0·1 to 0·15 gm. of the nitrite or nitrate, and for the larger one about 0·4 to 0·5 gm.

Hydrogen Peroxide.—The apparatus in this case is charged to the top of the measuring tube with a saturated solution of brine. 2 c.c. of hydrogen peroxide are introduced into the cup and then drawn carefully into the tube, so that no air is admitted. Any drops adhering to the side are rinsed into the tube with a little brine.

4 c.c. of copper ammonium sulphate solution are then admitted quickly but carefully. The mixture is well shaken

and allowed to stand for five minutes; the pressure is adjusted and the volume of oxygen read.
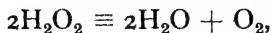
$$2H_2O_2 \equiv 2H_2O + O_2,$$
68 gm. of $H_2O_2 \equiv 22 \cdot 4$ litres of oxygen at S.T.P.,
$\therefore$ 1 c.c. of oxygen $\equiv$ 0·0030357 gm. of H_2O_2
$\equiv$ 0·3 per cent of H_2O_2 by weight, approx.*

The mechanism of the reaction is not clear, but it may be assumed that the cuprammonium sulphate solution acts as a solution of cuprous oxide, Cu_2O, the oxide acting catalytically in that it combines with the available oxygen of the peroxide, but the compound produced being immediately decomposed and the oxygen liberated.

Alternative Method.—Place in the decomposition flask 20 c.c. of decinormal potassium permanganate solution and 20 c.c. of dilute sulphuric acid. Into the inner tube pour 2 c.c. of hydrogen peroxide diluted with 10 c.c. of water. When these liquids are mixed the reaction is:

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4$$
$$= K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$
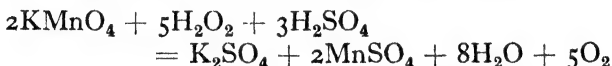
In this case, however,

1 c.c. of oxygen $\equiv$ 0·001518 gm. of H_2O_2 collected at S.T.P.

Potassium Permanganate.—The method for the estimation of permanganate is the converse of the alternative method for hydrogen peroxide. Excess of hydrogen peroxide is allowed to act on a known volume of permanganate solution in the presence of dilute sulphuric acid.

1 c.c. of oxygen at S.T.P. $\equiv$ 0·0028214 gm. of $KMnO_4$

Convenient quantities are 25 c.c. of a decinormal solution and 25 c.c. of dilute sulphuric acid placed in the decomposition flask, and 5 c.c. of hydrogen peroxide of 20 volume strength in the inner tube.

* For "Volume Strength" see J. Starck, *Volumetric Analysis*, p. 91.

Bleaching Powder.—Bleaching powder may be estimated by treatment with excess of hydrogen peroxide as described above. Half the total volume of the oxygen evolved is liberated by the chloride of lime. The reaction proceeds as follows:

$$CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2,$$
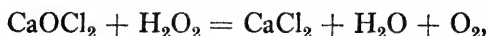
whence

127 gm. $CaOCl_2 \equiv$ 70·914 gm. of chlorine
$\equiv$ 22·4 litres of O_2,

∴ 1 c.c. oxygen at S.T.P.

$\equiv$ 0·00567 gm. of bleaching powder
$\equiv$ 0·003166 gm. of available chlorine.

Weigh out about 0·2 gm. of bleaching powder; introduce it into the flask and add 20 c.c. of water. Pour into the inner tube 5 c.c. of hydrogen peroxide. Connect to the nitrometer and allow the substances to interact; measure the volume of oxygen evolved.

Or, take 20 c.c. of the bleaching powder suspension made up as described below and proceed as above.

Weigh out about 2·5 gm. of fresh bleaching powder into a mortar, add water and triturate with a pestle. Transfer the thin cream to a 250 c.c. flask by means of a funnel. Continue the trituration with water until the whole has been transferred to the flask, wash the mortar and funnel thoroughly and make up to the mark. When it is desired to withdraw the bleaching powder solution the flask is thoroughly shaken and the requisite volume removed by means of a pipette before the powder has time to be deposited.

Spiritus Ætheris Nitrosi (Spirit of Nitrous Ether) (B.P. Method).—Introduce 2 c.c. into the nitrometer charged with brine, then 2 c.c. of potassium iodide solution and 2 c.c. of dilute sulphuric acid; shake vigorously at

intervals for five minutes and measure the volume of nitric oxide produced.

1 c.c. NO at 15·5° C. and S.P. $\equiv$ 0·0032 gm. of $C_2H_5O_2N$

Amyl Nitris (Amyl Nitrite) (B.P. Method).—Dilute 5 c.c. to 100 c.c. with 90 per cent alcohol. Use 2 c.c. of the diluted liquid and proceed as for Spiritus Ætheris Nitrosi:

1 c.c. NO $\equiv$ 0·0049 gm. of $C_5H_{11}O_2N$.

Halogens

These are estimated by the **Carius Method.**

The organic substance is oxidized by heating it with concentrated nitric acid at a high temperature and under pressure in the presence of a few crystals of silver nitrate. Under these conditions the carbon is completely oxidized to carbon dioxide and the hydrogen to water, while the halogen combines with the silver to form a silver halide; this is collected and weighed and the amount of halogen calculated in the ordinary way.

The experiment is conducted in a tube of combustion glass 40 cm. long and of bore 25 mm. 5 c.c. of concentrated nitric acid and about 5 gm. of silver nitrate crystals are placed in the tube, and a weighed amount (about 0·2 gm.) of the organic substance is introduced in a small glass test tube as shown (fig. 52). The open end of the tube is then drawn out into a thick-walled capillary and sealed.

Fig. 52.—Carius' Sealed Tube

The tube is then wrapped in a sheet of paper in order to prevent it cracking when inserted into the furnace, and

is placed in a stout iron tube fixed in a sheet iron furnace (fig. 53), where it is slowly heated to a temperature of about 300° C. and kept at that temperature for four to six hours. The decomposition gives rise to very high pressures which often break the glass tube; hence the furnace is made of iron. The furnace is allowed to cool down. The tube is then pulled out until about an inch of the capillary shows.
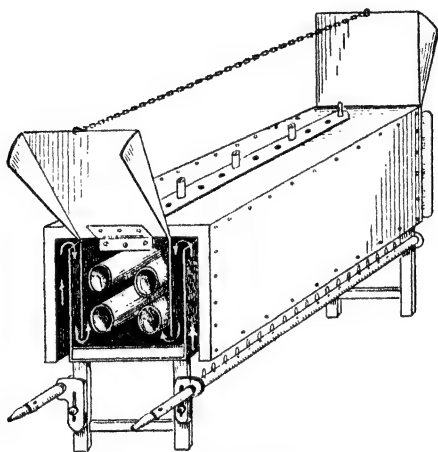

Fig. 53.—The Carius Furnace

The pointed end is cautiously heated until the glass is sufficiently soft to allow the gases inside to blow out; only at this stage is the tube entirely withdrawn. The contents are then washed out with distilled water into a beaker, and the solution is gently boiled for 15 min. The silver salt is filtered off on to a weighed Gooch crucible, well washed, dried in a steam oven, cooled and weighed. The percentage of halogen is estimated in the usual way:
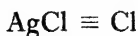
$$AgCl \equiv Cl$$
$$143\cdot347 \text{ gm. AgCl} \equiv 35\cdot457 \text{ gm. chlorine}$$

For practice: Estimate the halogen in (*a*) ethylene dibromide, (*b*) iodoform, (*c*) chlorobenzene.

Sulphur

The method employed is similar to that for the halogens, but no silver nitrate is included in the tube. The nitric acid oxidizes the sulphur to sulphuric acid, which is estimated by adding barium chloride solution to the contents washed out of the tube. The barium sulphate is filtered, washed, dried and weighed:

1 gm. $BaSO_4 \equiv$ 0·13735 gm. sulphur.

For practice: Use (*a*) thio-urea, (*b*) sulphanilic acid, (*c*) thiophene.

Phosphorus

This is estimated in a similar manner. The phosphorus present is converted into phosphoric acid, which can be estimated gravimetrically by precipitation as ammonium phospho-molybdate of composition $(NH_4)_3PO_4 \cdot 12MoO_3$:

1 gm. of this compound $\equiv$ 0·01653 gm. phosphorus.

For practice: Use (*a*) casein, (*b*) tri-ethyl phosphine.

QUESTIONS

1. 0·2315 gm. of an organic compound, containing only carbon, hydrogen and oxygen, gave on combustion 0·3395 of carbon dioxide and 0·1389 gm. of water. Calculate the empirical formula of the compound. Give the structural formulæ and the names of compounds of this composition containing one and two carbon atoms respectively. State briefly how each could be made and describe its more important reactions and properties.
(*I. M.B., London.*)

2. 10 c.c. of a hydrocarbon were mixed with 70 c.c. of oxygen (excess) and the mixture was sparked. The volume after explosion was 55 c.c., and this was reduced to 35 c.c. by treatment

with potash solution, all volumes being measured under the
same pressure and at the temperature of the laboratory. Deduce
the molecular formula of the gas.

(*Cambridge Higher School Cert.*)

3. 2 millilitres of a sample of Spirit of Nitrous Ether gave
when assayed by the official process 12·5 millilitres of nitric
oxide, measured at 14° C. and 745 mm. pressure; calculate the
percentage (weight in volume) of ethyl nitrite in the sample.
(Each millilitre of moist nitric oxide at 15·5° C., and normal
pressure is equivalent to 0·0032 gm. of $C_2H_5O_2N$).

(*Chemists and Druggists Qual.*)

4. 1·03 gm. of an organic liquid (A) produced on combustion
3·08 gm. of CO_2, 0·45 gm. of H_2O, and 112 c.c. of nitrogen
(measured at S.T.P.)

(A) was heated with a solution of sodium hydroxide; when
the product was acidified, a white crystalline precipitate (B) was
obtained, the solution of which was acidic.

When (B) was heated with lime it produced a volatile liquid
(C) whose vapour density was 39.

Deduce the formulæ of (A), (B) and (C) and explain the re-
actions.   (*Oxford Higher School Cert.*)

5. How would you detect the following elements in an organic
substance: nitrogen, sulphur, chlorine? Give an account of
either the Dumas or the Kjeldahl method of estimating nitrogen.

6. An organic compound on combustion gave the following
results: Carbon 20 per cent, hydrogen 6·67 per cent. By experi-
ment 0·1 gm. of the compound evolved 37·33 c.c. of dry nitrogen
measured at 0° C. and 760 mm. pressure. Calculate the empirical
formula of the compound. If the substance were non-volatile,
indicate briefly one method by which the molecular formula
could be determined.   (*Pre. Med.*)

7. An organic compound containing only carbon, hydrogen,
oxygen and nitrogen gave the following figures on analysis:
    0·1875 gm. of the compound gave 0·2200 gm. of carbon dioxide
and 0·1125 gm. of water.

0·2143 gm. of the compound gave 32·1 c.c. of nitrogen measured at 0° C. and 760 mm. pressure.

The molecular weight was found to be 75.

What is the molecular formula of the compound?

With sodium hydroxide a compound of empirical formula $C_2H_4O_2NNa$ is formed and with hydrochloric acid a compound of empirical formula $C_2H_6O_2NCl$.

What is the structural formula of the compound?

Give a brief account of its preparation (omitting experimental details). (*Cambridge Higher School Cert.*)

8. Describe and explain the method of carrying out the qualitative tests for the elements (*a*) Nitrogen, (*b*) Sulphur, (*c*) Halogens, in an organic compound.

Describe clearly one method for the quantitative determination of nitrogen in an organic compound. (*Prel. Sc.*)

9. 1·00 gm. of an organic compound, which consists of carbon, hydrogen, and nitrogen, produces on combustion 1·49 gm. of CO_2, 0·763 gm. of H_2O, and 190 c.c. of N_2 measured at S.T.P. . When heated with sodium hydroxide it yields ammonia and the sodium salt of an acid whose empirical formula is CH_2O.

When distilled with phosphorus pentoxide, it yields a liquid of the formula C_2H_3N, which, when hydrolysed, also produces ammonia and the same sodium salt.

When treated with bromine and potash, an alkaline gas of the formula CH_5N is evolved.

Explain these reactions, and write the structural formulæ of the compounds involved.

(C = 12, N = 14, O = 16, G.M.V. at S.T.P. = 22·4 litres).
(*Oxford Higher School Cert.*)

10. Describe, with full experimental details, Kjeldahl's method for the estimation of nitrogen in organic compounds. Name a class of nitrogenous organic compounds for which Kjeldahl's method is unsuitable.

11. An organic substance contained 17·75 per cent of carbon, 8·9 per cent of hydrogen, 52·5 per cent of chlorine and 20·75 per cent of nitrogen.

The substance when distilled with sodium hydroxide liberated an alkaline gas. 0·0596 gm. of this gas occupied 46·9 c.c. at 740 mm. and 17° C. Find the molecular formula of the substance and give an account of its reactions.

(Cambridge Higher School Cert.)

12. 0·1272 gm. of a liquid hydrocarbon gave, on combustion, 0·4257 gm. CO_2 and 0·0996 gm. H_2O. Its vapour density was found to be approximately 45. On oxidation, the hydrocarbon yielded an acid of the empirical formula $C_7H_6O_2$.

Identify the hydrocarbon and the acid, and write their structural formulæ.   *(Civil Service: Executive Group.)*

13. An organic substance gave the following results when quantitatively analysed by combustion:

Weight of substance $=$ 0·1237 gm.
Weight of CO_2 $=$ 0·4282 ,,
Weight of H_2O $=$ 0·0626 ,,

Calculate its empirical formula and, if possible, its molecular formula.

14. On combustion 0·2035 gm. of an organic compound, containing only carbon, hydrogen, and oxygen, gave 0·484 gm. of carbon dioxide and 0·2475 gm. of water. One litre of its vapour was found to weigh as much as 37 litres of hydrogen measured at the same temperature and pressure. Give the constitutional formula of the commonest compound of this composition and its molecular weight, and describe its preparation.

(Inter. B.Sc.)

15. Describe two methods for the quantitative determination of nitrogen in organic compounds.   *(B.Sc. London, General.)*

Identifications*

Ethyl Alcohol, C_2H_5OH, b. pt. 78° C.

1. Take 1 c.c. of alcohol in a boiling tube, fill one third of the tube with potassium dichromate and sulphuric acid mixture, let stand for five minutes; attach to the boiling tube a cork and a delivery tube bent downwards at an angle of 60°. Boil the mixture and pass the vapours into another boiling tube or test tube containing an inch of Schiff's reagent.

Notes.—(*a*) The potassium dichromate and sulphuric acid mixture is made up as follows. Weigh out 100 gm. of powdered potassium dichromate crystals in a 500 c.c. wide-mouthed glass stoppered bottle. Nearly fill the bottle with concentrated sulphuric acid. Close the bottle with the stopper and shake cautiously or allow to stand overnight. Use the clear solution for experimental purposes.

(*b*) *Preparation of Schiff's Reagent* (B.P. method).—Dissolve 1 gm. of magenta in 600 c.c. of hot water and cool; add 10 gm. of anhydrous sodium sulphite dissolved in 100 c.c. of water, followed by 10 c.c. of HCl; dilute to a litre and keep in a dark place when not in use.

(*c*) The above vapours should restore the pink colour of magenta.

2. Repeat Test 1 and pass the vapours into Tollen's reagent.

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* The following organic compounds have to be identified by pre-medical students.

Note.—(*a*) *Tollen's reagent* is prepared by taking about 3 c.c. of a 10 per cent solution of silver nitrate, adding one drop of sodium hydroxide, then ammonia drop by drop until a clear solution is obtained. Do not add excess of ammonia.

(*b*) Tollen's reagent must never be heated.

(*c*) An immediate grey-brown deposit of silver is obtained.

3. Repeat Test 1 and condense vapours in water in a test tube, just neutralize with ammonia, boil off any excess of ammonia and add ferric chloride. A red precipitate should be obtained, showing the presence of acetate.

4. *Iodoform reaction.*—This reaction is given by alcohols containing the group CH_3—$\overset{\displaystyle |}{\underset{\displaystyle |}{C}}$—OH, e.g. ethyl and iso-propyl alcohols.

Take about 2 c.c. of iodine solution, add one drop of ethyl alcohol, then sodium hydroxide solution carefully drop by drop until the colour of the iodine just disappears. A pale yellow precipitate of iodoform, CHI_3, forms either at once or on standing. This precipitate has a distinctive smell.

Detection of Methyl Alcohol in Industrial Spirit.

Repeat Test 1, using 5 c.c. of spirit, condense vapours in water, neutralize with ammonia (boil off excess), and divide the solution into four parts (*a*), (*b*), (*c*), (*d*). To

(*a*) Add 1 c.c. of silver nitrate solution and warm: brown solution and then a grey precipitate of silver;

(*b*) add mercuric chloride solution: white precipitate.

(*c*) add ferric chloride solution: wine-red colour; red-brown precipitate on warming;

(*d*) add a solution of potassium permanganate in sulphuric acid: pink colour discharged and a brown precipitate formed.

If all these tests are not given, then methyl alcohol is absent.

Formaldehyde, H · CHO

Take about 2 c.c. of strong formalin in a test tube and fill up with water, shaking well. Use this solution for the following tests:

1. Add 1 drop of the aldehyde to Schiff's reagent in a test tube: pink colour restored.

2. Add 2 or 3 drops to Tollen's reagent: a silver mirror or deposit is obtained.

3. Add 1 drop to 3 c.c. of Fehling's solution (equal parts of 1 and 2) and boil; red precipitate of cuprous oxide.

Preparation of Fehling's Solution.

Solution No. 1 is prepared by dissolving 69·28 gm. of pure copper sulphate crystals in distilled water and making the solution up to 1 litre.

. Solution No. 2 is prepared by dissolving 352 gm. of crystallized Rochelle salt (sodium potassium tartrate) in hot water. Cool and place in a litre flask, then add a cold solution of 154 gm. of sodium hydroxide and make up to 1 litre.

Notes.—(*a*) These solutions are kept separately; equal volumes are mixed when required.

(*b*) The above weights must be weighed out accurately when a quantitative estimation of a sugar is required (see p. 597).

4. Evaporate 3 c.c. of concentrated formalin on a clock glass over a beaker of boiling water. Note the white residue of paraformaldehyde. Heat a little of the paraformaldehyde in the bottom of a dry test tube, keeping the upper part cool by means of damp filter paper. Note the sublimate and smell of formaldehyde. Dissolve a little of the paraformaldehyde in water and test with Schiff's and Tollen's reagents.

5. Evaporate on a clock glass 5 c.c. of a mixture of equal volumes of concentrated formalin and concentrated ammonia solution. Small crystals of hexamine, $(CH_2)_6N_4$, are formed. Warm a little of the hexamine with dilute sulphuric acid; formaldehyde is regenerated. Boil off the formaldehyde; make the residual solution alkaline with sodium hydroxide and warm; ammonia is evolved (detected by its smell and action on damp red litmus paper).

6. Take 10 c.c. of the diluted solution in a porcelain basin, make just alkaline with NaOH, add 10 c.c. of hydrogen peroxide of 20 vol. strength, which has also been made just alkaline with NaOH. Warm on a beaker of boiling water for 5 minutes. Test with blue litmus paper. Make alkaline with ammonia and boil until neutral. Test the solution for formate with

(*a*) ferric chloride solution: wine-red colour; red-brown precipitate on warming;

(*b*) silver nitrate solution: brown solution; grey precipitate of silver on standing;

(*c*) mercuric chloride solution: white precipitate.

Colour Tests for Formaldehyde.

7. Add a drop of phenol solution to 3 c.c. of water and then add 3 or 4 drops of the diluted formalin. Now pour 2 c.c. of strong sulphuric acid from a test tube carefully down the side of the tube: a red ring is formed at the junction of the liquids.

8. Dissolve a trace of resorcinol in about 2 c.c. of water, and add 1 or 2 drops of dilute formalin. Now pour 2 c.c. of strong sulphuric acid carefully down the side of the tube; a violet-red ring is formed at the junction of the liquids. A white precipitate forms in the aqueous solution, changing to violet-red.

9. Add 1 drop of formalin to 100 c.c. of water. Then add 2 c.c. of a 1 per cent solution of phenylhydrazine hydro-

chloride and 1 c.c. of a 5 per cent solution of potassium ferrocyanide; shake well and add a few drops of strong hydrochloric acid: a rose-red tint is produced.

10. Add a few drops of sodium nitroprusside solution and a few drops of piperidine or a secondary base containing the group $=NH$: a deep blue colour is obtained.

Acetone, $CH_3 \cdot CO \cdot CH_3$, b. pt. 57° C.

1. Test with Schiff's reagent: no result at first, violet-red colour after a time.

2. Test with Tollen's reagent: no reduction.

3. Test with Fehling's solution: no reduction.

4. Try iodoform reaction (as for ethyl alcohol): positive.

5. Add a drop of acetone to about 3 c.c. of dilute sodium nitroprusside solution, then add sodium hydroxide solution: blood-red colour, turning violet-red when acidified with acetic acid.

6. Add a drop of mercuric chloride solution to about 3 c.c. of sodium hydroxide solution, then add one or two drops of acetone and shake: the yellow precipitate dissolves.

7. Shake 3 c.c. of acetone with twice its volume of a solution of sodium bisulphite (see below). Cool and shake vigorously; filter off the precipitate by suction in a Gooch crucible. Press down and allow to drain. Transfer the bisulphite compound to a 100 c.c. distilling flask, add a test-tubeful of sodium bicarbonate solution and distil until about one third of the volume has collected in the receiver. Test the distillate for acetone as above.

8. Add a few drops of *o*-nitrobenzaldehyde to a solution of acetone in sodium hydroxide: a blue indigo colour is produced.

Preparation of Sodium Bisulphite Solution.

Weigh out 350 gm. of sodium carbonate crystals and add 250 c.c. of water. Pass in sulphur dioxide and stir;

a precipitate of sodium bicarbonate is first formed, which ultimately disappears. Continue to pass in sulphur dioxide for about two hours, until the resulting solution is acid to litmus and smells of sulphur dioxide.

Acetic Acid, CH_3COOH, b. pt. 118° C., and Acetates

Note.—Tests with ferric chloride, silver nitrate, and calcium chloride mentioned under acids must be carried out with neutral solutions of salts. In the case of free acids make alkaline with ammonia and boil off the excess of ammonia until the solution is neutral to litmus.

1. Acetates boiled with dilute or concentrated sulphuric acid yield pungent vapours of acetic acid. Test with moistened blue litmus paper.

2. Acetates warmed with a little alcohol and concentrated sulphuric acid yield a fruity odour of ethyl acetate.

3. Ferric chloride solution with neutral acetate gives a wine-red colour. Divide solution into two portions (*a*) and (*b*): to

(*a*) Add dilute HCl: red colour changes to yellow;

(*b*) Boil: reddish-brown precipitate is produced.

4. Silver nitrate solution: no action.

5. Mercuric chloride solution: no action.

6. Potassium permanganate and dilute sulphuric acid mixture: no action.

7. Calcium chloride solution: no precipitate.

8. Heat alkali salt with arsenious oxide: odour of cacodyl, $As_2(CH_3)_4$ (poisonous).

Oxalic Acid, $(COOH)_2$, and Oxalates

1. Warm with concentrated sulphuric acid: carbon monoxide and carbon dioxide are evolved. (CO burns with a blue flame; test for CO_2 by lime water.) No charring results.

2. Silver nitrate solution: white precipitate with neutral solution of oxalate, soluble in dilute nitric acid.

3. Potassium permanganate and dilute sulphuric acid mixture: pink colour disappears on warming.

4. Calcium chloride solution: white precipitate with neutral solution of oxalate, insoluble in acetic acid but soluble in dilute hydrochloric acid and in nitric acid.

Lactic Acid, $CH_3CH \cdot (OH) \cdot COOH$, m. pt. $18°$ C., and Lactates

1. Warm with a little concentrated sulphuric acid: carbon monoxide is evolved and the acid quickly chars.

2. Boil with three times its bulk of 50 per cent sulphuric acid in a small distilling flask. Pass the vapours into water in a test tube. Test the solution for acetaldehyde with

(*a*) Tollen's reagent: precipitate of silver or mirror;

(*b*) Schiff's reagent: violet-red colour.

3. Ferric chloride solution gives a strong yellow colour with solutions of lactic acid or lactates. (Make a blank test for comparison by adding the same amount of ferric chloride solution to an equal volume of water.)

4. Silver nitrate: no precipitate with neutral solution.

5. Potassium permanganate and dilute sulphuric acid mixture: pink colour is destroyed on warming and a smell of acetaldehyde is perceptible.

6. Calcium chloride: no precipitate in neutral solution.

7. Gives iodoform reaction (as for ethyl alcohol). With calcium lactate a precipitate of calcium hydroxide is formed, which retains the iodoform precipitate.

Aceto-acetic Acid, $CH_3CO \cdot CH_2COOH$

This acid usually exists in the form of its esters, e.g. ethyl aceto-acetate, b. pt. $181°$ C.

1. Ferric chloride solution added to an alcoholic solution: violet colour.

2. Sodium hydroxide added to the ester: clear solution. On acidifying, the ester is reprecipitated.

3. Saturated copper acetate solution added to the ester: green crystalline precipitate.

4. NaOH or KOH at ordinary temperature added to the ester forms alkali salts. On acidifying and warming, carbon dioxide is evolved and acetone formed (test for acetone).

5. Dilute alcoholic potash added to the ester and boiled: acetone and potassium carbonate are formed. (Test for these two compounds.)

6. Concentrated alcoholic potash added to the ester and boiled: potassium acetate and ethyl alcohol are formed. (Test for these two compounds.)

7. Add hydroxylamine: presence of ketonic group $CO=$ is proved by formation of white oxime.

8. Add phenylhydrazine: presence of ketonic group $CO=$ is proved by formation of a phenylhydrazone.

9. Add prussic acid: presence of ketonic group $CO=$ is proved by formation of a cyanhydrin.

10. Add sodium bisulphite: presence of ketonic group $CO=$ is proved by formation of a bisulphite compound.

11. Add sodium nitroprusside to solution containing a little sodium hydroxide: a deep-red colour is produced.

Urea or Carbamide, $CO(NH_2)_2$, m. pt. 132° C.

1. *Biuret Test.*—Heat a little (0·5 gm.) solid urea over a small flame in a dry test tube until it melts and slowly evolves bubbles of ammonia (test with litmus paper and by its smell). Heat further until the liquid just solidifies; cool, dissolve in 10 c.c. of water, and add 1 c.c. of sodium hydroxide solution; add 1 drop of 10 per cent copper sulphate solution. A reddish-violet colour is produced. (B. P. Method).

2. Add a few drops of concentrated nitric acid to a fairly

concentrated urea solution: a white crystalline precipitate of urea nitrate is produced.

3. Repeat (2) using instead of nitric acid a concentrated solution of oxalic acid; a white precipitate of urea oxalate is produced.

4. Boil a little of the solid with sodium hydroxide solution: ammonia is evolved and sodium carbonate remains in the test tube. (Test for both these compounds.)

5. Dissolve a little urea in water, then add a little sodium nitrite solution and a few drops of dilute sulphuric acid. Warm gradually: carbon dioxide and nitrogen are evolved. (Test for CO_2.)

6. Add mercuric nitrate to urea solution: a white precipitate results.

7. Heat a little of the solid with sodium in an ignition tube: a derivative of cyanamide is formed. Extract with water and add a slight excess of ammonia and then silver nitrate solution: a yellow precipitate of silver cyanamide is formed.

8. Dissolve a little urea in 2 c.c. of sodium hydroxide solution, cool and add a few drops of sodium hypochlorite or hypobromite or, better still, a little bromine water and sodium hydroxide solution: rapid evolution of nitrogen occurs and sodium carbonate remains in the test tube. (Test for this compound.)

9. Repeat (5) but instead of using sodium nitrite add sodium hypobromite solution and dilute acid: carbon dioxide and nitrogen are evolved.

10. *Methyl furil test.*—Take a minute quantity of urea and mix it with an equal quantity of methyl furil solution in acetic acid and then add a drop of phosphorus oxychloride: a brilliant blue colour develops.

Glucose or Grape Sugar, $C_6H_{12}O_6$, m. pt. 144–146° C.

1. Add concentrated sulphuric acid: no charring results, but the sugar dissolves. On heating, the solution slowly blackens.

2. Add sodium or potassium hydroxide solution to a small quantity of glucose contained in a test tube and heat slowly: the solution turns first yellow, then brown.

3. Fehling's solution is reduced. Take 5 c.c. each of No. 1 and No. 2 Fehling's solution in a test tube, add a small quantity of glucose and warm gently; a bright red precipitate of cuprous oxide is formed.

4. Tollen's reagent is reduced. Make 3 c.c. of ammoniacal silver nitrate solution; add a small quantity of powdered glucose and place the test tube in a water bath and warm: a silver mirror is produced, provided the test tube is thoroughly clean.

5. Phenylhydrazine acetate is mixed with a dilute aqueous solution of glucose and heated on the water bath: a yellow crystalline precipitate of phenyl glucosazone is formed (m. pt. 204° C: see p. 352).

6. Action of yeast. Add a small pellet of yeast to a 10 per cent solution of glucose in a test tube. Fit this test tube with a cork containing a delivery tube which dips into another test tube containing lime water: carbon dioxide is evolved, turning the lime water milky. Note the smell of alcohol in the first test tube. This is a process of alcoholic fermentation.

7. Add picric acid to a solution of glucose in sodium hydroxide: a brown colour is obtained.

Phenol or Carbolic Acid, C_6H_5OH, m. pt. 42° C., b. pt. 182° C.

Phenol is slightly soluble in water; the aqueous solution is acid to litmus. It is readily soluble in sodium hydroxide,

but not in sodium carbonate solution. It is soluble in organic solvents.

1. *Liebermann's Reaction.*—Take a small crystal of phenol, dissolve it in 5 or 6 drops of concentrated sulphuric acid, add a trace of solid sodium nitrite and shake: a blue-green colour develops. Divide into two parts:

(*a*) Pour into water: a red colour results.

(*b*) Pour into caustic soda solution: a blue or green colour results.

2. Mix a little solid phenol with phthalic anhydride and a little concentrated sulphuric acid; make alkaline with sodium hydroxide: the red colour of phenol-phthalein is produced.

3. Ferric chloride solution added to (*a*) phenol solution gives a violet colour destroyed by acids. Mix with dilute ammonia and a little sodium hypochlorite or bleaching powder; a blue colour is produced. Ferric chloride added to (*b*) phenol neutralized by caustic soda gives a violet coloration.

4. Bromine water added to an aqueous solution of phenol gives a white precipitate of tribromophenol, $C_6H_2(OH)Br_3$.

5. *Picric acid test.*—Dissolve a little phenol in an equal weight of concentrated sulphuric acid. Warm gently, then add this mixture gradually to about twice its volume of strong nitric acid; shake well and warm. Pour the mixture into cold water: yellow crystals of picric acid (trinitrophenol), $C_6H_2OH(NO_3)_3$, separate. Filter, recrystallize from dilute hydrochloric acid, dry, and take the melting-point of the picric acid (122° C.).
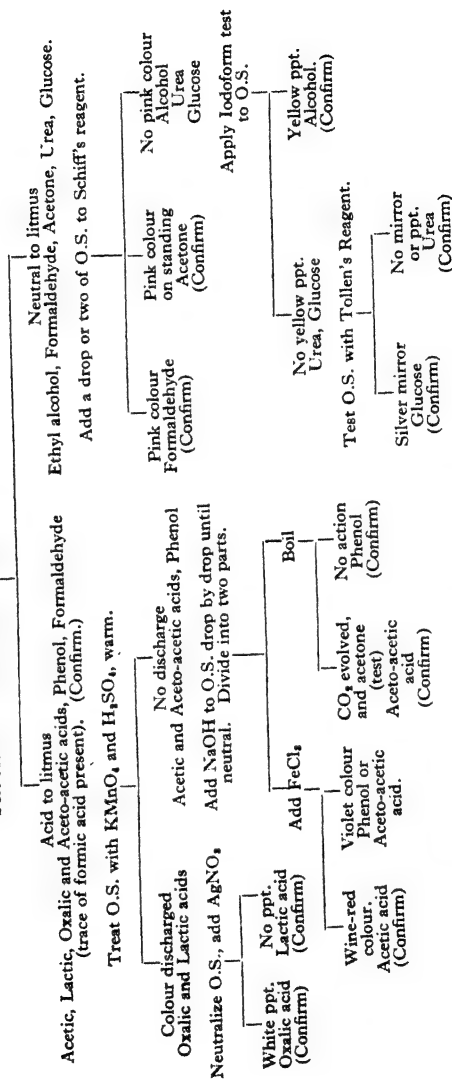
6. *Schotten-Baumann Reaction* (formation of benzoyl derivative).—Dissolve a little phenol in caustic soda solution; add twice the bulk of benzoyl chloride and shake well. Then add excess of caustic soda and leave until the smell of benzoyl chloride disappears. Dilute with water, filter, and wash well with water. Recrystallize from alcohol, dry well and take the melting-point (68° C.) of the phenyl benzoate, $C_6H_5CO \cdot OC_6H_5$.

SUMMARY OF IDENTIFICATIONS OF ORGANIC SUBSTANCES
(FOR PRE-MEDICAL STUDENTS)

Liquids: Ethyl alcohol, Formaldehyde, Acetone, Acetic, Lactic and Aceto-acetic acids.

Solids: Oxalic acid, Urea, Glucose and Phenol.
All soluble in water except Aceto-acetic ester.
Test solution with blue litmus paper.

Acid to litmus
Acetic, Lactic, Oxalic and Aceto-acetic acids, Phenol, Formaldehyde
(trace of formic acid present). (Confirm.)

Treat O.S. with $KMnO_4$ and H_2SO_4, warm.

- **Colour discharged**
  Oxalic and Lactic acids

  Neutralize O.S., add $AgNO_3$
  - **White ppt.**
    Oxalic acid
    (Confirm)
  - **No ppt.**
    Lactic acid
    (Confirm)

- **No discharge**
  Acetic and Aceto-acetic acids, Phenol

  Add NaOH to O.S. drop by drop until neutral. Divide into two parts.

  - Add $FeCl_3$
    - **Violet colour**
      Phenol or Aceto-acetic acid.
      - **Wine-red colour.**
        Aceto-acetic acid
        (Confirm)
    - **Boil**
      - **CO_2 evolved, and acetone** (test)
        Aceto-acetic acid
        (Confirm)
      - **No action**
        Phenol
        (Confirm)

Neutral to litmus
Ethyl alcohol, Formaldehyde, Acetone, Urea, Glucose.

Add a drop or two of O.S. to Schiff's reagent.

- **Pink colour**
  Formaldehyde
  (Confirm)

- **Pink colour on standing**
  Acetone
  (Confirm)

- **No pink colour**
  Alcohol
  Urea
  Glucose

  Apply Iodoform test to O.S.

  - **Yellow ppt.**
    Alcohol.
    (Confirm)

  Test O.S. with Tollen's Reagent.

  - **No yellow ppt.**
    Urea, Glucose
    - **Silver mirror**
      Glucose
      (Confirm)
    - **No mirror or ppt.**
      Urea
      (Confirm)

Notes.—1. Many of these substances have a characteristic odour.
2. All confirmatory tests are to be conducted with original solution or substance (O.S.).

CHAPTER XXIII

Additional Identifications

1. Alcohols

Oxidation Test. Primary Alcohols yield the Aldehyde and the Acid.

Take 1 c.c. of the alcohol in a test tube, fill up the tube with potassium dichromate and sulphuric acid mixture (p. 525), pour into a small distilling flask and allow to stand for five minutes. Distil, using a water condenser, until about half the volume has passed over. Divide the distillate into two parts:

(*a*) Test for aldehyde with Schiff's and Tollen's reagents. Also try tests for particular aldehydes (p. 541 et seq.).

(*b*) Make alkaline with ammonia, boil to remove the aldehyde and excess of ammonia, and test for acids with the solution of the neutral salt thus obtained (pp. 544, 555).

Try the oxidation test with:

1. Methyl Alcohol (b. pt. 65° C.).

(*a*) Test distillate with Schiff's and Tollen's reagents and also for formaldehyde by the resorcinol and concentrated sulphuric acid test (p. 528).

(*b*) Test neutral ammonium salt for formate with ferric chloride and mercuric chloride solutions and by warming with aqueous silver nitrate (p. 544).

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2. **Ethyl Alcohol** (absolute) (b. pt. 78° C.).

(*a*) Test distillate with Schiff's and Tollen's reagents, also by warming with sodium hydroxide solution to show formation of aldehyde resin.

(*b*) Test neutral ammonium salt for acetate with $FeCl_3$, &c. (p. 530) and also for formate (p. 544).

(*c*) Try other tests for acetaldehyde as outlined on p. 541.

Note.—Commercial methyl alcohol generally contains some acetone, and hence may give the iodoform test. Pure methyl alcohol does not give it.

Other primary alcohols include *n*-propyl (b. pt. 97° C.), *n*-butyl (b. pt. 117° C.), iso-butyl (b. pt. 107° C.), and iso-amyl (b. pt. 131° C.) alcohols. These yield aldehydes which are sparingly soluble or insoluble in water and lighter than water. They distil over and react with both Schiff's and Tollen's reagents on shaking.

Normal propyl alcohol is readily soluble in water; the others are sparingly soluble and float on water.

Oxidation Test. Secondary Alcohols yield Ketones.

Carry out the above oxidation test with isopropyl alcohol (b. pt. 81° C.). This alcohol is readily soluble in water. Test the distillate for acetone by the nitroprusside test (p. 529). The result is negative, but with sodium nitroprusside and caustic soda an intense yellow colour is obtained; moreover, no acetate test is given with $FeCl_3$.

Try iodoform test with distillate.

2. Esters

(by examination of the products of hydrolysis)

Take 1 c.c. of the ester in a test tube and add a little 20 per cent caustic potash solution; a white precipitate indicates immediate hydrolysis (e.g. with amyl salicylate).

General Procedure.

Weigh out approximately 10 gm. of the ester in a CO_2 flask, add 50 c.c. of a 20 per cent KOH solution and a few pieces of porous pot to prevent bumping. Boil gently under a reflux condenser.

Notes.—1. If ester gives an immediate precipitate with KOH, heat the potash solution before adding the ester, then boil for 10 minutes to complete the hydrolysis.

2. If ester is soluble in KOH solution, boil for 15 minutes.

3. If ester is insoluble in KOH solution:

(*a*) With esters of soluble alcohols, e.g. methyl, ethyl, *n*-propyl, isopropyl, allyl alcohols, in most cases the layer will disappear in 15 minutes to 1 hour.

(*b*) With esters of insoluble or sparingly soluble alcohols, e.g. *n*-butyl, isobutyl, iso-amyl, benzyl alcohols, the layer will never completely disappear. Boil 1 hour. In most cases such esters are completely hydrolysed in this time. Then connect the flask to a sloping condenser and distil over about one third of the original volume.

I. If the distillate is clear, test for methyl, ethyl, *n*-propyl, isopropyl and allyl alcohols by the oxidation and iodoform tests.

II. If the alcohol is insoluble, separate it from the water by a small separating funnel, dry with anhydrous potassium carbonate and take the boiling-point of the alcohol. Also try the oxidation test.

Notes.—(*a*) *n*-butyl, isobutyl and iso-amyl alcohols float on water; benzyl alcohol is heavier than water.

(*b*) If the alcohol does not distil over readily (e.g. benzyl alcohol) return the distillate to the flask, cool and transfer to a small separating funnel, shake with ether. Run off the alkaline solution, wash the ethereal layer three times with water, separate from the water and distil off the ether from the water bath.

Treatment of Residue in Flask.

Add dilute nitric acid to about 1 c.c. in a test tube, cool and shake.

(*a*) If a precipitate separates (benzoic, salicyclic, cinnamic, phenyl-acetic, phthalic acids, &c.), acidify the whole of the residue in the flask with dilute nitric acid. Filter off the precipitate, wash well with cold water, crystallize from alcohol, dry in desiccator, take the melting-point and apply special tests.

(*b*) If no precipitate separates, add sulphuric acid (1 : 2) until the residue in the flask is just acid, then add ammonia until alkaline, cool and filter off the potassium sulphate.

Crystalline soluble acids (e.g. oxalic acid) may separate with the potassium sulphate. Keep this precipitate in order to test for such acids. Boil the filtrate until neutral, cool some of this solution and apply tests with $FeCl_3$, $CaCl_2$, $AgNO_3$, &c., and endeavour to identify the acid present (pp. 544, 555).

Evaporate the remainder in a basin until spirting commences, then complete the evaporation on a sand bath, holding the basin with a pair of tongs and stirring rapidly until all the water is removed. Test the solid salt with concentrated H_2SO_4, &c.

3. Aldehydes

Try the following general reactions with an aqueous solution of formaldehyde or acetaldehyde, prepared as follows:

Formaldehyde.—Take about 2 c.c. of concentrated formaldehyde solution (formalin) in a test tube and fill up with water.

Acetaldehyde.—Distil 2 c.c. of paraldehyde with a test-tubeful of dilute H_2SO_4 (bench acid) from a small distilling flask connected to a water condenser.

General Tests for Aldehydes.

1. Add a drop of the aldehyde solution to about 3 c.c. of Schiff's reagent (1 in. deep in a test tube). Allow to stand; a violet-red colour is produced. (Schiff's reagent must never be heated, as this drives off SO_2 and restores the original magenta colour.)

2. Add a drop or two of Tollen's reagent (p. 526) to the aldehyde solution; a mirror or deposit of silver is formed.

3. Add a drop of the formaldehyde solution to about 3 c.c. of Fehling's solution (equal parts of solutions 1 and 2, p. 527), and boil; a red precipitate of Cu_2O is formed.

In the test with acetaldehyde, take 3 c.c. of the mixed Fehling's solution, dilute to a test-tubeful with water, take 3 c.c. of this solution, add a little of the acetaldehyde solution and boil. First there is a green colour, then a red precipitate of Cu_2O; the solution is yellow, owing to formation of aldehyde resin.

4. Add a little aldehyde solution to a mixture of equal parts of $KMnO_4$ and Na_2CO_3 solutions, shake and allow to stand. The purple colour disappears and a brown precipitate is formed.

Special Tests for Formaldehyde (see p. 527, Tests 4–10).

Special Tests for Acetaldehyde (b. pt. 20·8° C.).

1. Add a drop or two of the aqueous solution to about 3 c.c. of iodine solution, then add sodium hydroxide solution drop by drop until the colour of the iodine just disappears. Warm gently or allow to stand; a yellow precipitate of iodoform is formed.

2. Warm a little aldehyde solution with sodium hydroxide solution; a yellow colour is formed, then an orange precipitate of aldehyde resin, with a disagreeable odour.

3. Test as for formaldehyde with phenol solution and concentrated sulphuric acid; a reddish-brown ring forms at the junction of the liquids.

4. Ketones

1. Schiff's reagent; some ketones, e.g. acetone, give the violet-red colour, but much more slowly than aldehydes do.

✗ 2. Tollen's reagent and Fehling's solution are not reduced.

Special Tests for Acetone (see p. 529, Tests 4–6).

Methyl ethyl ketone (b. pt. 81° C.) gives the same reactions as acetone, but in the nitroprusside test the bloodred colour is unaltered by acetic acid.

Preparation of Bisulphite Compounds of Aldehydes and Ketones.

1. Shake about 1 c.c. of benzaldehyde with five times its bulk of sodium bisulphite solution (p. 529). Filter off the precipitate by suction, press down the precipitate in the funnel with a spatula and drain off any liquid as completely as possible. Note that the smell of benzaldehyde has disappeared. Warm a little of the bisulphite compound with sodium carbonate solution; benzaldehyde (recognized by its smell) is regenerated.

2. Proceed as described under Acetone, test 7, p. 529.

Add sodium bisulphite solution to:

(*a*) **Acetophenone,** $C_6H_5CO \cdot CH_3$: no action and no heat generated.

(*b*) **Anisaldehyde,** $C_6H_4(OCH_3)CHO$ (*para*): scarcely any heat is developed; the bisulphite compound comes down clean after a little vigorous shaking. Filter and wash with ether. Treat the compound with boiling sodium carbonate solution; the aldehyde separates as an oil, being insoluble in water.

(c) **Salicylaldehyde,** $C_6H_4(OH) \cdot CHO$ (*ortho*): scarcely any heat is developed. The bisulphite compound comes down clean after vigorous shaking, requiring rather longer than anisaldehyde. Filter and wash with ether. Treat the compound with hot sodium carbonate solution; a yellow solution is obtained, since this aldehyde is slightly soluble in water.

(d) **Cyclohexanone,** $C_6H_8O_2$: scarcely any heat is developed. The bisulphite compound is formed immediately. Filter off and wash the white precipitate with ether. Treat the compound with hot sodium carbonate solution; there is no separation, as this compound is soluble in water. A peppermint odour is observed.

(e) **Cinnamic Aldehyde,** $C_6H_5CH : CH \cdot CHO$: scarcely any heat is developed. There is an immediate yellow precipitate, but it may be obtained white by transferring this bisulphite compound to a beaker and stirring round with ether. Filter and repeat the process. On adding hot sodium carbonate solution the aldehyde separates as an oil and the solution is coloured yellow.

(f) **Furfural,** $C_4H_3O \cdot CHO$: heat is developed. The aldehyde dissolves in the bisulphite solution, but no precipitate is obtained on cooling or on standing.

(g) **Piperonal,** $C_6H_3 : CH_2O_2 \cdot CHO$. Dissolve this compound in ether and shake with bisulphite solution; a precipitate is readily formed. Filter, wash with ether and treat the bisulphite compound with hot sodium carbonate solution; the aldehyde separates as an oil which solidifies on cooling (m. pt. 37° C.).

(h) **Vanillin,** $C_6H_3(OH)(OCH_3)CHO$, (4 : 3). Treat like Piperonal; no precipitate is formed.

5. Organic Acids and their Salts

Notes.—1. Tests with $FeCl_3$, $AgNO_3$ and $CaCl_2$ must be carried out with **neutral solutions** of salts. In the case

of free acids or acid salts make alkaline by adding a slight excess of ammonia and boil until neutral to litmus.

2. **Treatment of Insoluble Salts.**—First test whether the salt is soluble or insoluble. If insoluble, proceed as follows:

Mix the salt with an equal bulk of dry sodium carbonate and boil with water for 10 minutes. Filter, acidify filtrate with dilute nitric acid, then make alkaline with ammonia, boil off excess of ammonia until neutral. Test neutral solution of sodium salt of the organic acid with $FeCl_3$, $CaCl_2$, $AgNO_3$, &c.

Formic Acid, b. pt. 101° C., and **Formates** (H · COOH).

1. Take a little solid formate in a test tube, just cover it with concentrated sulphuric acid and warm. Turn the mouth of the tube to the flame; carbon monoxide is evolved, which burns with a blue flame; no charring observed.

Concentrated solutions of formic acid heated with an equal bulk of concentrated sulphuric acid act similarly.

2. Formates warmed with dilute sulphuric acid yield pungent fumes of formic acid. Test with moistened blue litmus paper.

3. Formates or formic acid warmed with aqueous silver nitrate yield a brown solution, and finally a grey precipitate of silver.

4. Tollen's reagent; no reduction.

5. $HgCl_2$; add 2 or 3 drops to a solution of a formate or formic acid and warm: a white precipitate of mercurous chloride is formed.

6. $CaCl_2$: no precipitate with neutral solution of a formate.

7. $FeCl_3$, with neutral formate solution, gives a wine-red colour.

Divide solution into two portions:

(*a*) Boil: a reddish brown precipitate is formed.

(*b*) Add dilute HCl: the red colour changes to yellow.

8. $KMnO_4$ and dilute H_2SO_4 solution are added to formic acid and formates and heated: the permanganate is reduced and a brown precipitate formed. A clear colourless solution is obtained only on prolonged boiling with excess of formate.

Acetic Acid and Acetates (CH_3COOH).

Tests for these are given on p. 530.

Salts of Palmitic, Stearic, and Oleic Acids.

The sodium and potassium salts of these acids are soluble in hot water. On the addition of dilute HCl the free acids are precipitated. Stearic and palmitic acids are solids at the ordinary temperature, but melt in hot water. Oleic acid is a liquid at ordinary temperatures.

$CaCl_2$ added to solution of alkali salt gives a precipitate of the calcium salt.

Insoluble salts are decomposed by dilute HCl, yielding the free acids.

Tests for Unsaturation of Oleic Acid.

1. Add oleic acid to bromine dissolved in carbon tetrachloride: the solution is decolorized.

2. Shake with equal parts of $KMnO_4$ and Na_2CO_3 solutions: the purple colour disappears and a brown precipitate is obtained.

Note.—This reaction is given by other easily oxidizable compounds such as formates, aldehydes, alcohols.

Lactic Acid and Lactates.

Tests for these are given on p. 531.

Oxalic Acid and Oxalates.

Tests for these are given on p. 530.

Tartaric Acid, COOH · CHOH · CHOH · COOH (m. pt. 170° C.) and **Tartrates.**

1. Warm solid with concentrated sulphuric acid:

(*a*) alone: carbon monoxide is evolved, but is not so easy to detect as with a lactate. The solid chars readily.

(*b*) with a trace of resorcinol: a violet-red colour is produced.

(*c*) with a trace of β-naphthol: a green colour is produced, turning orange on dilution with water.

2. $CaCl_2$ added to neutral tartrate solution gives a heavy white crystalline precipitate on vigorous shaking, soluble in hot dilute acetic acid, and also soluble in cold concentrated NaOH solution. If the caustic soda solution is boiled the calcium tartrate is reprecipitated, but dissolves again on cooling.

For this test to be successful the supernatant liquid is decanted off and the precipitate is washed with water, allowed to settle again, and the supernatant liquid again decanted off. If this is not done the excess of calcium chloride present is precipitated by the caustic soda.

3. $AgNO_3$ with neutral solution: heavy white precipitate on standing, soluble in excess of alkaline tartrate and in dilute HNO_3. Pour off supernatant liquid and add very dilute ammonia drop by drop until the precipitate just dissolves. Place the test tube in a hot water bath: a silver mirror forms.

4. Tollen's reagent: no reduction.

5. $FeCl_3$ gives a strong yellow colour, as with lactic acid.

6. $KMnO_4$ and dilute H_2SO_4: the solution is decolorized on warming.

7. *Fenton's Test.*—Take 5 c.c. of the dilute solution, add a trace of powdered ferrous sulphate, then one drop of H_2O_2 (20 volume strength); the solution should darken. Then add excess of NaOH: an intense violet colour is produced.

8. KCl in concentrated solution shaken with free tartaric acid gives a heavy white crystalline precipitate of potassium hydrogen tartrate. (Neutral tartrates must be acidified with acetic acid for this test.)

9. Tartaric acid and tartrates in sufficient quantity prevent the precipitation of cupric hydroxide, &c., from solutions of the corresponding salts.

Citric Acid, $COOH \cdot CH_2 \cdot C(OH)(COOH) \cdot CH_2 \cdot COOH$ (m. pt. 153° C.) and **Citrates.**

1. Warm solid gently with concentrated sulphuric acid: carbon monoxide is evolved. A yellow solution is obtained, which on further heating becomes brown, then black.

2. $CaCl_2$ added to neutral solution of a citrate gives no precipitate in the cold, but a crystalline precipitate on boiling. This precipitate is insoluble in caustic soda.

3. $AgNO_3$ with neutral solution of citrate gives an immediate white precipitate. Just dissolve precipitate in ammonia and place the test-tube in boiling water: a deposit of silver or a mirror is produced.

4. Tollen's reagent: no reduction.

5. $FeCl_3$ gives a strong yellow colour with free citric acid or citrate solutions.

6. $KMnO_4$ and dilute H_2SO_4 are decolorized on warming.

7. *Denigès' Test.*—Add about 1 c.c. of Denigès' solution, which is made by dissolving yellow mercuric oxide in sulphuric acid (1 : 4), to about 3 c.c. of citric acid or citrate solution. Heat to boiling, then add one drop of permanganate solution: the purple colour disappears and a white precipitate forms suddenly.

8. Similar to test 9 for Tartrates (above).

Benzoic Acid, C_6H_5COOH (m. pt. 121° C., b. pt. 249° C., eq. wt. 122) and **Benzoates.**

1. Warm with concentrated H_2SO_4: benzoic acid and benzoates give white sublimate; solution turns brownish.

2. Warm with absolute alcohol and a few drops of strong H_2SO_4: a pleasant smell of ethyl benzoate is observed.

3. $CaCl_2$ gives no precipitate with neutral benzoate solutions.

4. $AgNO_3$ gives a white crystalline precipitate which is soluble in hot water, but crystallizes out on cooling.

5. $FeCl_3$ gives a buff precipitate with neutral solutions of benzoates.

6. Mix with 3 times its bulk of powdered soda lime and heat: benzene is evolved, and tested for, as follows:

Place the mixture of benzoic acid and soda lime in a test tube, then add a layer of coarse soda lime about 1 in. deep. Attach to the mouth of the tube a cork fitted with a bent tube. Rest this test tube on a tripod, allowing the end of the delivery tube to dip into a dry test tube standing in a beaker of cold water.

Heat the coarse soda lime first and then the mixture. Collect the distillate and to it add a few drops each of concentrated nitric and sulphuric acids. Dilute with water; the bitter-almond smell of nitrobenzene is observed.

7. Concentrated hydrochloric acid precipitates benzoic acid from concentrated solutions of benzoates. Filter off the precipitate by suction, wash with cold water, crystallize from the smallest possible quantity of alcohol, dry in a steam oven, and take the melting-point.

Salicylic Acid, $C_6H_4OH \cdot COOH$ (m. pt. 155° C., eq. wt. 138) and Salicylates.

1. Warm with concentrated H_2SO_4: there is little or no sublimate, and a reddish-brown solution is obtained.

2. Warm with methyl alcohol and concentrated H_2SO_4: the smell of methyl salicylate is observed (more apparent when the test tube is filled with water). A red solution is obtained.

3. $CaCl_2$
4. $AgNO_3$ } give the same reactions as for benzoates.
5. HCl

6. Salicylic acid gives a violet colour with a drop of $FeCl_3$; salicylates a blood-red colour, turning violet with excess of $FeCl_3$. The violet colour is not discharged by acetic acid.

7. Heat with three times its bulk of dry powdered soda lime: a smell of phenol is observed.

Succinic Acid, $COOH \cdot CH_2 \cdot CH_2 \cdot COOH$ (m. pt. 185° C., eq. wt. 59), and **Succinates.**

1. $CaCl_2$ gives no precipitate.

2. $AgNO_3$ gives white precipitate with neutral succinate solution.

3. $FeCl_3$ gives a bulky cinnamon-brown precipitate with neutral succinate solution.

. 4. Warm gently with twice its bulk of resorcinol and 2 or 3 drops of concentrated sulphuric acid until the mixture assumes a deep red colour. Cool, dilute carefully, and make alkaline with caustic soda: a red solution is obtained, showing a yellow-green fluorescence on dilution with water.

Phthalic Acid, $C_6H_4(COOH)_2$ (m. pt. 195–213° C. (decomposes), eq. wt. 83) and **Phthalates.**

1. $CaCl_2$ gives no precipitate.

2. $AgNO_3$ added drop by drop gives a white precipitate which redissolves in the solution, but is permanent with excess of $AgNO_3$. Dilute solutions give a precipitate only on standing.

3. $FeCl_3$ added drop by drop gives a reddish-brown solution, then a buff precipitate. In dilute solutions only a red-brown colour is obtained.

4. H_2SO_4 and resorcinol give the same reaction as succinic acid.

5. Warm with an equal bulk of phenol and two or three drops of concentrated H_2SO_4 until the mixture has a deep red colour. Cool, dilute carefully and make alkaline with caustic soda: the red colour of phenol-phthalein is produced.

6. Concentrated hydrochloric acid precipitates phthalic acid from concentrated solutions of phthalates.

Phenyl-Acetic Acid, $C_6H_5 \cdot CH_2COOH$ (m. pt. 76° C., b. pt. 262° C., eq. wt. 136).

Tests 1–4 should be performed with a neutral solution of the ammonium salt.

1. $CaCl_2$ gives no precipitate.

2. $AgNO_3$ gives a curdy gelatinous precipitate, soluble in hot water.

3. $FeCl_3$ gives a buff precipitate.

4. HCl precipitates the acid.

5. Heat free acid with solid $KMnO_4$ and dilute H_2SO_4: a smell of benzaldehyde is observed.

Cinnamic Acid, $C_6H_5CH : CH \cdot COOH$ (m. pt. 133° C., b. pt. 299° C., eq. wt. 148).

Tests 1–4 should be performed with a neutral solution of the ammonium salt.

1. $CaCl_2$ gives a precipitate, but not immediately; a white precipitate forms quickly on shaking, and is soluble in hot water, crystallizing out again on cooling.

2. $AgNO_3$ gives a white precipitate.

3. $FeCl_3$ gives a yellow precipitate.

4. HCl precipitates the acid.

5. Dissolve cinnamic acid in alcohol, and add to bromine water: the brown colour slowly disappears.

6. Add a little cinnamic acid to $KMnO_4$ and Na_2CO_3 solutions mixed in equal quantities, and shake well:

reduction takes place quickly in the cold, with a smell of benzaldehyde; on warming the smell is intensified.

7. Boil cinnamic acid with $K_2Cr_2O_7$ and 10 per cent sulphuric acid; it is oxidized to benzoic acid. Cool, filter, and dissolve crystals in boiling water. Filter hot and allow filtrate to cool. Benzoic acid crystals are deposited. Filter off these crystals, dry, then take the melting-point.

6. Monohydric Phenols

These are slightly soluble in water, and their aqueous solutions are acid to litmus. They are readily soluble in NaOH, but not in Na_2CO_3 solution.

Phenol (aqueous solution).

Ferric chloride gives violet colour. Bromine water gives white precipitate. For other tests, see p. 535.

Ortho-Cresol (m. pt. 31° C., b. pt. 190° C.).

Ferric chloride gives blue colour with aqueous solution; other tests as for phenol.

Meta-Cresol (liquid) (b. pt. 202° C.).

Ferric chloride gives blue colour. Phthalein test gives violet colour.

Liebermann's reaction (p. 535): not decisive.

Para-Cresol (m. pt. 35° C., b. pt. 201° C.).

Ferric chloride gives blue colour. Phthalein test gives no colour in cold.

Liebermann's reaction: not decisive.

α- and β-Naphthols (α m. pt. 94° C., b. pt. 278° C., β m. pt. 122° C., b. pt. 285° C.).

These are soluble in hot water, only slightly in cold. Test with aqueous solution.

1. With ferric chloride α gives white precipitate with one drop. Add four or five drops and leave to stand: violet colour develops.

β gives pale green colour, white precipitate on standing.

2. Add iodine solution and excess of caustic soda:

α gives violet colour, β no colour.

3. Add solution in NaOH to diazotized aniline (made by dissolving a drop of aniline in dilute HCl and adding a few drops of sodium nitrite solution):

α gives dark red precipitate, β bright red precipitate.

Phenols are identified by conversion into crystalline acetyl or benzoyl derivatives with definite melting-points.

Preparation of Acetyl Derivative.

Just cover with acetic anhydride and heat for 10 minutes in a small flask with an air condenser. Pour into water and allow to solidify. Filter on porcelain plate in glass funnel, and dissolve in a small quantity of alcohol, then filter through a fluted filter into a small beaker and leave to crystallize. Dry in a desiccator over concentrated sulphuric acid, then take the melting-point.

(Use β-naphthol.)

Preparation of Benzoyl Derivative.

Dissolve phenol in NaOH and add twice the bulk of benzoyl chloride and shake well. Add excess of NaOH and leave until the smell of benzoyl chloride disappears. Dilute with water, filter and wash well with water. Crystallize from alcohol.

(Prepare phenyl benzoate from phenol and take its melting-point, (68° C.)).

7. Di- and Trihydric Phenols

These are readily soluble in water.

They all reduce Tollen's reagent (distinction from mono-hydric phenols.)

Catechol (m. pt. 104° C., b. pt. 245° C.).

1. The solution in NaOH is green or red.
2. Silver nitrate gives grey precipitate.
3. Ferric chloride gives green colour, turning red with ammonia.
4. Lead acetate gives white precipitate.

Quinol (m. pt. 169° C.).

1. Forms yellowish-brown solution with alkalis, darkening on exposure to air.
2. Silver nitrate is reduced in the cold.
· 3. Ferric chloride gives blue colour, quickly changing to a brown solution. Heat: a pungent smell of quinone is noticed. Cool: green needles of quinhydrone separate.
4. Potassium dichromate and dilute sulphuric acid, on heating and subsequent cooling, give yellow needles of quinone.
5. Lead acetate gives no precipitate. Add a drop or two of ammonia: a yellowish-white precipitate is formed.

Resorcinol (m. pt. 118° C., b. pt. 276° C.).

The solution in NaOH oxidizes in the air, giving a yellowish-green solution.

1. Ferric chloride gives violet colour.
2. Silver nitrate gives no action.
3. Tollen's reagent is slowly reduced.
4. Lead acetate gives no precipitate.
5. Fluorescein test: see under phthalic and succinic acids.

6. Warm with tartaric acid and concentrated sulphuric acid: a reddish-violet colour is produced.

7. Dissolve in NaOH, add to diazotized aniline: a red dye is formed.

Pyrogallol (m. pt. 133° C., b. pt. 293° C.)

1. NaOH gives dark red colour.

2. Ferric chloride gives blue colour, quickly changing to red.

3. Ferrous sulphate gives blue-violet colour, more intense on shaking or adding a trace of ferric chloride.

4. Silver nitrate is immediately reduced.

5. Lead acetate gives white precipitate.

Acetyl and benzoyl derivatives may be prepared by methods similar to those employed for monohydric phenols.

QUESTION

D is a solution of an aldehyde in an alcohol. Separate the mixture and leave on your bench purified specimens of the alcohol and the aldehyde. Record the boiling point in each case. (E.g. benzaldehyde in ethyl alcohol.)

(*B.Sc. London, General.*)

CHAPTER XXIV

Examination for Organic Acids
and their Salts

After the tests for organic acids and their salts have been
worked through, the following scheme may be found useful
for identifying an organic acid or salt given as an " unknown "
substance.

General Tests.

A. With solid substance.

1. Boil with dilute HCl. Stearates, palmitates and oleates
yield insoluble free acids as oils floating on the surface of
the liquid. These have a characteristic smell. On cooling
palmitic and stearic acids solidify, oleic acid remains liquid.

Free palmitic and stearic acids melt in hot water, yielding
insoluble oils floating on the surface.

The acid nature of free palmitic, stearic and oleic acids
is seen on dissolving them in alcohol, adding phenol-
phthalein and then alcoholic potash drop by drop.

Soluble salts of the fatty acids form a lather with water.
For further details, see pp. 545, 605 *et seq.*

If no oily products are obtained on boiling with dilute
HCl, proceed as follows:

2. Place a little of the solid in a dry test tube, just cover
with concentrated H_2SO_4 and warm gently. Turn the
mouth of the tube to the flame; if carbon monoxide is
evolved, it will burn with a blue flame.

Formates, oxalic acid and **oxalates.** Carbon

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monoxide is evolved readily, no charring; concentrated solutions of formic acid (liquid) heated with an equal bulk of concentrated H_2SO_4 behave similarly.

Lactates. Char quickly: carbon monoxide is readily evolved.

Lactic acid (thick liquid). Acts similarly.

Tartaric acid and **tartrates.** Char quickly, smell of burnt sugar; carbon monoxide is evolved, but not readily.

Citric acid and **citrates.** Yellow solution is formed, carbon monoxide is readily evolved; on further heating the solution turns brown and then black.

Benzoic acid and **benzoates.** White sublimate is formed.

Salicylic acid and **salicylates.** May give white sublimate.

3. Heat with dilute H_2SO_4.

Formates and **acetates** yield pungent fumes with characteristic smell, turning moistened blue litmus paper red. The same applies to aqueous solutions of the salts or the free acids.

4. If substance is soluble in water, test solution (*a*) with blue litmus paper, (*b*) by adding it to water reddened with phenol-phthalein and a drop of dilute NaOH solution.

Acid reaction indicates free acid or acid salt.

Neutral reaction indicates neutral salt.

5. Heat solid with NaOH solution. **Ammonium salt** is indicated by evolution of ammonia, detected by its smell and by blue colour given to moistened red litmus paper held in escaping vapours.

6. *To distinguish between Free Acid and Metallic Acid Salt.*

Just cover the bottom of a crucible with the solid, moisten with 50 per cent H_2SO_4, using a dropping tube. Place on a pipe-clay triangle on a tripod and heat until dry, using a

very small flame ($\frac{1}{2}$ in. high). If the dry charred mass swells up, press it down into the bottom of the crucible with a glass rod. Heat to redness until all the carbon has burnt away.

Residue (white in most cases) indicates metallic salt. No residue indicates free acid (or ammonium salt).

7. *Preparation of a Neutral Solution of a Salt of the Acid.*

(*a*) If the substance is a soluble neutral salt, simply dissolve it in distilled water.

(*b*) If the substance is a soluble acid or acid salt, dissolve in distilled water, add ammonia until alkaline (stir round and test with red litmus paper), and boil until perfectly neutral (test with red litmus paper), adding distilled water if necessary.

(*c*) If the substance is insoluble in water, or sparingly soluble, add an equal bulk of dry Na_2CO_3 and distilled water; boil for 10 minutes. Filter off the solid, if any (filtrate should be alkaline), acidify the filtrate with dilute HNO_3, stir round and test with blue litmus paper, make alkaline with ammonia, stir round and test as in (*b*).

B. To solution of neutral salt of acid, add:

1. $FeCl_3$ solution, drop by drop.

Formate, acetate give a wine-red colour with excess of $FeCl_3$. Divide into two portions:

(*a*) Add dilute HCl: the red colour changes to yellow.

(*b*) Boil: a reddish-brown precipitate is formed.

Lactate, tartrate, citrate, glycollate and **hydroxyacids** give strong yellow colour. (Do a blank test by adding the same amount of $FeCl_3$ to an equal volume of water.)

Benzoate, phenyl acetate: a buff precipitate is formed.

Phthalate gives a reddish-brown solution, then a buff precipitate (with dilute solution only a red-brown colour).

Salicylate gives blood-red colour, violet with excess, not discharged by acetic acid.

Cinnamate gives yellow precipitate.
Succinate gives bulky cinnamon-brown precipitate.
Gallate gives dark-blue colour.

2. $CaCl_2$ solution.

Formate, acetate, lactate, benzoate, salicylate, succinate, phthalate, phenyl acetate give no precipitate.

Oxalate gives immediate white precipitate (unless very dilute), not settling rapidly, insoluble in hot water or acetic acid. If no immediate precipitate, shake vigorously or allow to stand, or scratch tube with a glass rod.

Cinnamate gives crystalline white precipitate, soluble in hot water.

Tartrate gives heavy white crystalline precipitate, moderately soluble in hot dilute acetic acid, soluble in cold concentrated KOH or NaOH.

To test solubility in NaOH, allow precipitate to settle, pour off supernatant liquid, shake with water, allow precipitate to settle again, and decant off supernatant liquid. (Otherwise a precipitate will be formed by the action of the NaOH on the $CaCl_2$ present.) The precipitate is readily soluble in 20 per cent NaOH; and in bench reagent on shaking. If no precipitate is formed on shaking or standing, boil well.

Citrate gives a white crystalline precipitate, soluble in hot acetic acid and insoluble in cold concentrated NaOH. Test solubility as for Tartrate.

3. $AgNO_3$ solution, drop by drop, finally excess; if no immediate precipitate is formed, shake vigorously or allow to stand.

Formate, acetate, lactate give no precipitate, unless formate or lactate is very concentrated.

Oxalate, citrate, succinate, cinnamate, tartrate,

phthalate, benzoate, salicylate, phenyl acetate give a white precipitate.

Phthalate and **tartrate** give white precipitate redissolving in excess of alkaline solution, but if excess of $AgNO_3$ has been added the precipitate is permanent.

Benzoate, salicylate and phenyl acetate give white precipitate soluble in hot water.

If tartrate or citrate is indicated by the previous tests, allow precipitate to settle, pour off supernatant liquid, just dissolve precipitate in very dilute ammonia and place test tube in boiling water. Silver mirror or deposit indicates **tartrate** or **citrate.**

If no precipitate is obtained on shaking or standing, heat the solution: a brown colour, finally a grey precipitate of silver, indicates **formate** (distinction from acetate).

4. Concentrated HCl.

. **Benzoate, salicylate, phthalate, cinnamate, phenyl acetate:** the free acid is precipitated from concentrated solutions. Filter off the precipitate by suction, wash carefully with cold water, drain as dry as possible, transfer a little to a watch glass, dry in steam oven and take melting-point.

(M. pts. benzoic 121° C., salicylic 155° C., phenyl-acetic 76° C., cinnamic 133° C., phthalic 195–213° C.)

5. Heat with $KMnO_4$ and dilute H_2SO_4.

Oxalate, tartrate, citrate. Solution is decolorized.

Lactate. Solution is decolorized and the smell of acetaldehyde is observed.

Formate, phenyl acetate, cinnamate give brown precipitate.

The mixture froths if the original solid substance is heated with solid $KMnO_4$ and dilute H_2SO_4 in a boiling tube.

Cinnamate, phenyl acetate. Smell of benzaldehyde (bitter almonds) is observed.

This test may be carried out with the original solid substance.

Determination of the Equivalent Weight of an Organic Acid

In the identification of an acid its equivalent weight should always be determined as follows:

Method 1.—**Volumetrically** by titration with standard sodium hydroxide, using phenol-phthalein as indicator.

It is assumed that the student is familiar with the methods of standardizing acids and alkalis; if not, he should make himself familiar with acidimetry and alkalimetry.*

(*a*) *Standardization of an approximately N/10 NaOH solution.*

The NaOH should be standardized by means of standard N/10 HCl. The acid is first standardized against pure sodium bicarbonate. Phenol-phthalein must always be used as the indicator when the sodium hydroxide is to be used for the titration of organic acids.

The alkali can also be standardized by means of pure succinic acid, the equivalent weight of which is 59. Weigh out accurately about 0·2 gm. of the acid, transfer to a conical flask and titrate directly.

0·2 gm. succinic acid will neutralize $\dfrac{1000}{59} \times$ 0·2 c.c. N · NaOH = 3·39 c.c.

Find the factor of the alkali from the formula:

$$\frac{1000}{59} \times \frac{\text{Weight of acid taken}}{\text{Volume of alkali}}.$$

The factor should be stated in terms of normal solution.

* See e.g. H. P. Starck, *Volumetric Analysis*, Chapter IV.

(*b*) Weigh out accurately in a weighing bottle from 0·2 to 0·6 gm. of the organic acid. If it is soluble in water wash into a conical flask with distilled water. If it is only sparingly soluble in cold water, wash into the flask with neutralized alcohol, using a small wash bottle kept specially for alcohol. (The alcohol is neutralized by adding phenol-phthalein, then N/10NaOH drop by drop until a faint pink colour is obtained after shaking.)

The solution of acid is then titrated with N/10 NaOH in the presence of phenol-phthalein until a permanent red tint remains after shaking.

Calculate the weight of acid corresponding to 40 gm. of NaOH; this will be the equivalent weight of the acid.

Example.—Weight of acid taken = 0·3 gm.
This required 37·9 c.c. of NaOH (factor 0·0964N).

37·9 × 0·0964 c.c. N · NaOH neutralize 0·3 gm. of acid.

∴ 1 c.c. N · NaOH neutralizes $\dfrac{0·3}{37·9 \times ·0964}$ gm. of acid.

∴ 1000 c.c. N · NaOH neutralize $\dfrac{0·3 \times 1000}{37·9 \times 0·0964} = 82·1$.
(40 gm.)

∴ Equivalent weight of acid = 82·1.

Method 2.—**Gravimetrically** by ignition of silver salt (use benzoic acid).

Prepare a neutral solution of the ammonium salt of the acid by dissolving the acid in ammonia, making sure that the solution is alkaline to litmus, then ·boiling until neutral to litmus. Cool, and add silver nitrate solution. Filter off the precipitate of the silver salt by suction, wash three times with distilled water, sucking dry each time. Finally wash twice with alcohol, then twice with ether, and dry in a desiccator.

Weigh out accurately about 0·5 gm. of this salt in a

crucible. Heat very carefully on the top first until all organic matter has burnt away, otherwise the salt spirts out. Finally heat strongly until only a whitish residue of silver is left. Cool in a desiccator and weigh. Repeat until weight is constant.

Calculate the weight of silver salt equivalent to 108 gm. of silver.

To obtain the equivalent weight of the acid subtract 108 for one atom of silver and add 1 for the atom of hydrogen which it has replaced.

QUESTIONS

1. Write a careful account of what you would do in the laboratory in order to determine the molecular weight of an organic acid of unknown composition.

2. By what properties would you distinguish a formate from an acetate? From acetic acid how would you prepare a specimen of (a) acetyl chloride, (b) acetic anhydride, (c) phenyl acetate?

3. Explain how you could identify in as many ways as possible a solution of (a) glucose, (b) cane sugar, (c) starch, (d) formaldehyde.

4. Hydrolyse about 10 grams of the substance A by means of the alkali provided. Describe anything you notice during hydrolysis. From the product of hydrolysis prepare a crystalline specimen of an acid and leave it for examination. Determine (a) the melting point of the acid, (b) the equivalent weight of the acid by titration with standard alkali provided. (E.g. ethyl benzoate, benzyl salicylate).   (*II. M.B., London.*)

Compounds Containing Nitrogen

(A) Ammonium Salts and Acid Amides

It is assumed that nitrogen has been detected in the test for elements, either by the evolution of ammonia on heating with soda lime or by the sodium test (p. 492). Now proceed as follows:

1. Add a little cold NaOH solution to the substance. Test for ammonia by smell or by holding a piece of damp red litmus paper in the tube, taking care not to let it touch the side of the tube.

· NH_3 is readily evolved in the cold by ammonium salts of acids.

Acid amides may give off ammonia slowly in the cold.

2. Heat with NaOH. Ammonia is readily evolved from ammonium salts and acid amides.

Comparison of Ammonium Salts and Acid Amides.

(*a*) Ammonium salts are usually readily soluble in water; the corresponding acid amide is often only sparingly soluble in water.

(*b*) Aqueous solutions of acid amides do not, as a rule, give the tests for acids with $FeCl_3$, $CaCl_2$, &c.

(*c*) When warmed with concentrated or boiled with dilute sulphuric acid, amides give the same results as ammonium salts, since they are hydrolysed.

Note.—**Formamide,** $HCONH_2$ (a liquid), resembles **ammonium formate,** $HCOONH_4$, in its behaviour with cold NaOH and $FeCl_3$ and when heated with aqueous

$AgNO_3$ and with $HgCl_2$ (p. 544). It gives carbon monoxide with concentrated H_2SO_4.

3. To identify an acid amide, boil with NaOH solution, acidify with dilute nitric acid, make alkaline with ammonia and boil until neutral.   Test the neutral solution with $FeCl_3$, $CaCl_2$, $AgNO_3$, &c.

Cool some of the neutral solution and acidify with concentrated HCl. If an acid separates, filter off, recrystallize (usually from alcohol), dry and take the melting-point.

The differences and resemblances between ammonium salts and acid amides are illustrated by the following examples.

Ammonium Acetate, CH_3COONH_4, and Acetamide, CH_3CONH_2.

Both are crystalline hygroscopic substances readily soluble in water. Acetamide usually smells of mice.

1. $FeCl_3$ added to aqueous solutions gives red colour with ammonium salt, but not with amide.

2. Dilute H_2SO_4 added and boiled: both substances give vapours of acetic acid, which turn moistened blue litmus paper red.

3. NaOH: (*a*) In cold solutions ammonium salts evolve ammonia readily, whereas amides evolve ammonia only very slowly.

(*b*) In hot solutions ammonia is readily evolved from both.

4. Boil acetamide with NaOH, acidify with dilute HNO_3 (test with litmus paper), then make alkaline with ammonia (test with litmus paper), boil till neutral (again test), cool, and add $FeCl_3$: a red colour is produced.

Ammonium Oxalate, $(COONH_4)_2$, and Oxamide, $(CONH_2)_2$.

Ammonium oxalate is a crystalline substance soluble in water. Oxamide is a white powder sparingly soluble in boiling water. It sublimes on heating.

1. Concentrated H_2SO_4: no charring; both evolve carbon monoxide.

2. $KMnO_4$ and dilute H_2SO_4 are decolorized by both substances, but with oxamide much more slowly.

3. NaOH: (a) In cold solutions ammonia is evolved readily from the ammonium salt, but only very slowly from oxamide.

(b) In hot solutions ammonia is readily evolved from both.

4. $CaCl_2$: (a) Boil oxamide with water and filter. Add $CaCl_2$ to hot solution: no precipitate.

(b) $CaCl_2$ added to ammonium oxalate solution gives immediate white precipitate insoluble in acetic acid.

5. Boil oxamide with NaOH, then proceed as for acetamide, test 4. To neutral solution add $CaCl_2$: white precipitate is formed.

6. Colour test for oxamide: add 1 c.c. NaOH to a little oxamide and then 1 drop of copper sulphate solution, shake well: red colour is formed.

Ammonium Benzoate, $C_6H_5COONH_4$, and Benzamide, $C_6H_5CONH_2$.

The ammonium salt is readily soluble in cold water, whereas benzamide is sparingly soluble in cold water, but readily soluble in hot water.

1. Concentrated H_2SO_4 added to solid and warmed: both substances give a white sublimate of benzoic acid.

2. NaOH: (a) In cold solutions ammonia is evolved readily from the ammonium salt, but only very slowly from benzamide.

(b) In hot solutions ammonia is readily evolved from both.

3. $FeCl_3$ added to aqueous solution of ammonium salt gives buff precipitate. No precipitate with benzamide.

4. Concentrated HCl and ammonium salt give white precipitate of benzoic acid. No precipitate in the cold with benzamide.

5. Boil benzamide with NaOH solution, then proceed as for acetamide, test 4. Divide neutral solution into two portions.

(*a*) Add $FeCl_3$: a buff precipitate is formed.

(*b*) Add a little concentrated HCl, filter off precipitated benzoic acid and recrystallize from alcohol, dry and take the melting-point (121° C.).

Ammonium Phthalate, $C_6H_4(COONH_4)_2$, and Phthalamide, $C_6H_4(CONH_2)_2$.

The ammonium salt is readily soluble in water, whereas phthalamide is practically insoluble in both cold and hot water.

Try the following tests with phthalamide:

1. Phthalein test as for phthalic acid (test 5, p. 550).

2. Fluorescein test as for phthalic acid (test 4): a greenish-brown colour is produced.

3. NaOH: ammonia is evolved slowly in cold solution, readily when heated.

4. Boil phthalamide with NaOH solution, then proceed as for acetamide, test 4. To neutral solution add $FeCl_3$: a buff precipitate results.

5. Boil with water, cool and filter. Add $FeCl_3$ to filtrate: a buff precipitate results.

6. The substance is practically insoluble in ether.

Ammonium Succinate $(CH_2COONH_4)_2$, and Succinamide $(CH_2CONH_2)_2$.

The ammonium salt is readily soluble in water, whereas succinamide is sparingly soluble in cold water but readily in hot water.

Try the following tests with succinamide:

1. Fluorescein test as for succinic acid (test 4, p. 549).

2. NaOH added and solution warmed: ammonia is evolved.

3. Boil with NaOH solution, then proceed as for acetamide (test 4, p. 564). To neutral solution add $FeCl_3$: a bulky cinnamon-brown precipitate is obtained.

4. Heat with zinc dust. In the fumes of pyrrole evolved hold a wooden match moistened with concentrated HCl: a red colour is formed after a short time. This test is also given by the ammonium salt and by succinimide.

5. The substance is insoluble in ether.

Urea, $CO(NH_2)_2$, m. pt. 132° C. See tests, p. 532.

Other simple compounds which yield ammonia with NaOH include **Imides, Aldehyde ammonias, Urethanes** and **Nitriles.**

If ammonia is not evolved on heating, boil the substance with dilute sulphuric acid, noting the smell of the vapours evolved, then make alkaline with sodium hydroxide and test for ammonia.

· Aldehydes will be liberated from their compounds with ammonia; volatile acids from amides and nitriles.

For complete hydrolysis, boil with dilute sulphuric acid, using a reflux condenser.

Urethanes.—On boiling with NaOH they yield, in addition to ammonia, sodium carbonate and an alcohol.

Ethyl Urethane, $NH_2COOC_2H_5$, is soluble in water; boil with NaOH under a reflux condenser and test the solution for

(a) sodium carbonate by adding H_2SO_4: CO_2 is evolved (tested with lime water);

(b) ethyl alcohol by iodoform test (p. 526).

Hexamine $(CH)_2N_4$.

1. Dilute H_2SO_4 added and boiled: a smell of formaldehyde is observed. Pass the vapours into water and apply tests for formaldehyde (p. 527).

2. To solution left from (1) add NaOH until alkaline and heat: ammonia is evolved (tested with moistened red litmus paper).

Determination of the Equivalent Weight of an Amide

Weigh out accurately about 1 gm. of the amide and transfer to a conical flask. (This should be done by finding the difference in the weight of a weighing bottle before and after transferring the amide to the flask.) Add about 40 c.c. of N · NaOH from a burette, running the alkali down the neck of the flask so as to wash any amide down to the bottom. Heat for 10 min. and shake round until all the amide has dissolved, then add about 100 c.c. of distilled water and boil vigorously for 15 min. to remove ammonia. (The steam is tested with moistened red litmus paper.) When no more ammonia is evolved, cool the solution, add phenol-phthalein as indicator and " back titrate " with N · HCl.

Calculate the amount of amide which has reacted with 40 gm. of NaOH. This gives the equivalent weight of the amide.

Example.

Weight of oxamide taken = 1·0056 gm.
Amount of NaOH taken = 42 c.c. Factor = 1·036.
Amount of HCl taken = 20 c.c. Factor = 1·025.
Number of cubic centimetres
  of N · NaOH added   =42 × 1·036 = 43·51 c.c.
Excess of N · NaOH added = 20 × 1·025 = 20·5 c.c.

                    Volume used   23·01 c.c.

23·01 c.c. N · NaOH react with 1·0056 gm. of oxamide.

1000 c.c. N· NaOH react with $\dfrac{1·0056}{23·01} \times 1000 = 43·7$.
  (40 gm.)

        Equivalent weight of oxamide = 43·7.

(B) **Primary Aromatic Amines** ($-NH_2$ in nucleus)

I. General Tests.

1. Take 1 c.c. if the substance is a liquid, or 1 gm. if a solid, and add dilute HCl until a clear solution is obtained. Heat if necessary, but cool afterwards. To the clear solution, add NaOH until alkaline (test with red litmus paper). Allow to stand: if a precipitate is formed, an amine is present.

2. *Carbylamine Test.*—This test must be carried out in a fume cupboard, and the carbylamine must be immediately destroyed by pouring on concentrated HCl.

Add one drop of aniline to about 2 c.c. of alcoholic potash in a test tube; then add 2 or 3 drops of chloroform and warm gently: the intolerable smell of phenyl carbylamine is produced.

3. *Diazo-Test.*—Add 3 or 4 drops of aniline or other base to about 4 c.c. of dilute HCl in a test tube, then add about 1·c.c. of dilute sodium nitrite solution and shake. Divide the solution into two portions.

(*a*) Pour into about 5 c.c. of alkaline β-naphthol, made by dissolving a little β-naphthol in sodium hydroxide solution: an intensely coloured precipitate of an azo-dye is obtained.

Aniline and many other common bases give a red dye.

(*b*) Boil: nitrogen is evolved and a phenol formed (detected by its smell).

II. Identifications.

The following preparations serve to identify these amines (aniline (p. 445) is taken as an illustration):

Method 1.—**Preparation of a Salt of the Base** (usually the hydrochloride).

Preparation of the Hydrochloride.—Take 5 c.c. of redistilled aniline (about ¼ test-tubeful) in a beaker and add three times its volume of concentrated HCl and stir.

Cool and filter off by suction. Press the salt down with a spatula and allow to drain for a time. Stop the suction and moisten the salt all over with acetone. Allow to stand for a few minutes and drain off. Repeat the washing with acetone twice and drain as dry as possible. Place the salt on a clock glass in a desiccator and leave to dry in a dark place.

Notes.—1. Do not dry in a steam oven, as the salt is liable to become discoloured.

2. If the base is solid (e.g. *p*-toluidine), boil with 50 per cent HCl until it dissolves. Filter through a filter paper if the solution is not perfectly clear, and cool.

Determination of Equivalent Weight of Base

The salt is then analysed by one of the following methods.

A. Volumetrically:

Weigh out accurately about 0·5 gm. of the hydrochloride in a weighing bottle. Wash the salt with distilled water into a 250 c.c. flask, using a funnel. Add 2 or 3 drops of phenolphthalein as indicator and titrate with N/10 NaOH until a permanent red colour is obtained after shaking; or, better, use N/10 Ba(OH)$_2$ solution. (0·5 gm. of aniline hydrochloride requires exactly 38·6 c.c. N/10 NaOH).

Example.

Weight of aniline hydrochloride taken = 0·5012 gm.

Amount of NaOH required = 37·55 c.c.   Factor = 0·103.

Number of c.c. N · NaOH required = 37·55 × 0·103 c.c.

Since 37·55 × 0·103 c.c. N · NaOH ≡ 0·5012 gm. hydrochloride, then

$$1000 \text{ c.c. of N} \cdot \text{NaOH} \equiv \frac{0.5012 \times 1000}{37.55 \times 0.103} = 129.5.$$
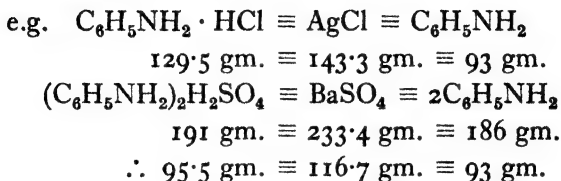$$(40 \text{ gm.})$$

Equivalent weight of hydrochloride = 129·5.

∴ Equivalent weight of base

= (C$_6$H$_5$NH$_2$ · HCl) — (HCl) = 129·5 — 36·5 = 93.

B. Gravimetrically:

The acid present in a small weighed (0·25–0·5 gm.) quantity of the salt of a base may be precipitated by means of $AgNO_3$, $CaCl_2$ or $BaCl_2$ solutions and weighed as $AgCl$, $CaCO_3$, $BaSO_4$, or $BaCO_3$.

e.g. $C_6H_5NH_2 \cdot HCl \equiv AgCl \equiv C_6H_5NH_2$

$$129·5 \text{ gm.} \equiv 143·3 \text{ gm.} \equiv 93 \text{ gm.}$$

$$(C_6H_5NH_2)_2H_2SO_4 \equiv BaSO_4 \equiv 2C_6H_5NH_2$$

$$191 \text{ gm.} \equiv 233·4 \text{ gm.} \equiv 186 \text{ gm.}$$

$$\therefore 95·5 \text{ gm.} \equiv 116·7 \text{ gm.} \equiv 93 \text{ gm.}$$

Method 2.—**Preparation of the Acetyl Derivative** (Acetanilide) (see p. 459).

Take about 2 c.c. of redistilled aniline in a small beaker and add to it 3 c.c. of acetic anhydride, very gradually, as the mixture becomes very hot. Then add about 75 c.c. of water and stir. Boil and stir until the acetyl derivative is dissolved. Cool, filter off by suction, wash with cold water and dry in the steam oven.

Notes.—(*a*) Take the melting-point of the dry solid.

(*b*) When a solid base is given, warm gently until a clear solution is obtained.

(*c*) Primary amines should not be boiled with acetic anhydride, as a diacetyl derivative may be formed.

(*d*) The equivalent weight of the base may be found by boiling the acetyl derivative with concentrated HCl. Hydrolysis occurs; the acetic acid formed is driven off and the hydrochloride left is titrated as in Method 1.

Repeat using α-naphthylamine.

Method 3.—**Preparation of the Benzoyl Derivative** (Benzanilide).

Put 1 c.c. of aniline into a 250 c.c. flask and add about 5 c.c. of acetone and 1·5 c.c. of benzoyl chloride from a burette. To this mixture add slowly, a little at a time, 50 c.c. of bench NaOH with constant shaking until the solid

benzoyl derivative separates, then add the remainder of the NaOH. Cork tightly and shake the contents well until the smell of benzoyl chloride disappears. Cool, filter by suction, pressing down with a spatula. Wash three times with hot water, drain as dry as possible.

Transfer the benzanilide to a small beaker and just cover with alcohol. Heat the beaker in hot water until the benzanilide is dissolved, adding more alcohol if necessary. Cool, filter off the crystals by suction, press down, wash with a few drops of cold alcohol, drain as dry as possible, and finish the drying in a steam oven. Take the melting-point of the solid.

The equivalent weight of the base may be determined by boiling the benzoyl derivative with hydrochloric acid; benzoic acid and the hydrochloride of the base are formed.

$$C_6H_5CO \cdot NH \cdot C_6H_5 + HOH + HCl = C_6H_5COOH + C_6H_5NH_2 \cdot HCl$$

Benzanilide		Benzoic acid	Aniline hydrochloride
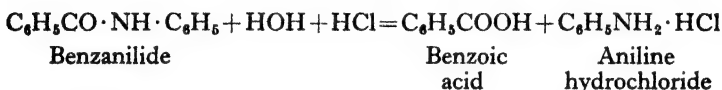
These may be separated by treatment with hot water, which dissolves the benzoic acid. The solution is filtered hot and the hydrochloride washed into hot water. The benzoic acid is then titrated with standard alkali; or the hydrochloride is estimated as under Method 1.

Method 4.—**Preparation of the double salt of the base with $PtCl_4$ or $AuCl_3$:**

e.g. $$(C_6H_5NH_2)_2H_2PtCl_6.$$
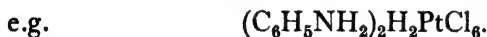
A weighed quantity of the double salt (0·25–0·5 gm.) is ignited in a weighed porcelain crucible and the residue of platinum or gold weighed.

$$Pt \equiv (C_6H_5NH_2)_2H_2PtCl_6 \equiv 2C_6H_5NH_2$$

$$195 \cdot 23 \text{ gm.} \equiv 596 \cdot 11 \text{ gm.} \qquad \equiv 186 \cdot 12 \text{ gm.}$$

$$\therefore 97 \cdot 615 \text{ gm.} \equiv 298 \cdot 055 \text{ gm.} \qquad \equiv 93 \cdot 06 \text{ gm.}$$

QUESTIONS

1. Indicate the composition of the following reagents and discuss by reference to particular tests the purposes for which they are used:

(*a*) Fehling's solution;

(*b*) Mayer's reagent *;

(*c*) Schiff's reagent.

(Cheismts and Druggists Qual.)

2. (*a*) Describe in detail how you would test qualitatively an organic substance for the presence of nitrogen and explain the chemistry of your method.

(*b*) Describe briefly the action of heat on *four* of the following:

(1) A mixture of benzoic acid and soda lime.

(2) A mixture of calcium acetate and calcium formate.

(3) A mixture of aqueous sodium hydroxide and a fat.

(4) Silver acetate.

(5) Sodium formate.

(Cambridge Higher School Cert.)

* See p. 636

CHAPTER XXVI

Preparations

Preparation of Salts of Organic Acids

The metals which are most commonly found in combination with the organic acids are: Lead, Silver, Calcium, Barium, Sodium, Potassium; and the Ammonium group. Other metals may, however, be found.

1. Salts of Sodium, Potassium or Ammonium.

(a) *The neutral salts* can be prepared by neutralizing the organic acid with a solution of NaOH, KOH, or NH$_4$OH and evaporating until crystallization takes place.

(b) *The acid salts* of the dibasic acids may be prepared by neutralizing a weighed quantity of the acid (or a measured volume of its solution) with NaOH, KOH or NH$_4$OH, and then adding an equal weight of the acid (or an equal volume of its solution). Heat to dissolve, or evaporate, as necessary.

(c) *Neutral and acid salts of the polybasic acids* may be prepared by mixing equivalent quantities of the organic acid and the carbonate or bicarbonate of sodium or potassium. Heat to dissolve completely, filter and set aside to crystallize:

e.g.
$$\begin{matrix} \text{COOH} \\ | \\ \text{COOH} \end{matrix} \cdot 2H_2O + Na_2CO_3 = \begin{matrix} \text{COONa} \\ | \\ \text{COONa} \end{matrix} + 3H_2O + CO_2$$

Oxalic acid   Sodium oxalate
126 gm.   106 gm.

$$2 \begin{matrix} \text{COOH} \\ | \\ \text{COOH} \end{matrix} \cdot 2H_2O + Na_2CO_3 = 2 \begin{matrix} \text{COONa} \\ | \\ \text{COOH} \end{matrix} + 5H_2O + CO_2$$

126 gm.   53 gm.   Sodium hydrogen
                                          oxalate
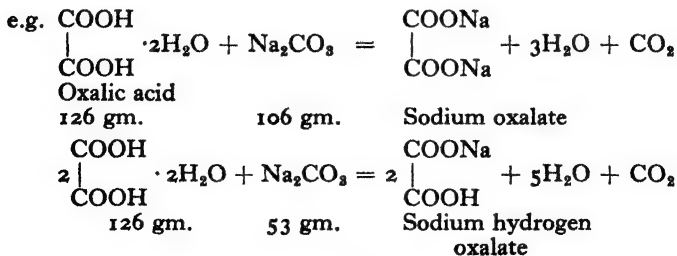
2. **Salts of other Metals,** e.g. Ag, Pb, Ca, Ba.

Since the method of preparation depends upon the solubility of the salt, the student should always proceed as follows:

Carefully neutralize a very small quantity of the organic acid with ammonia; this is done by adding a slight excess of ammonia and boiling off the excess until neutral. Then add a solution of the salt of the metal whose organic salt is required (e.g. $AgNO_3$, $Pb(NO_3)_2$, $Pb(acet)_2$, $CaCl_2$, $BaCl_2$.)

Cool and note what happens. If a precipitate forms, heat the liquid to boiling, and see whether the precipitated salt is soluble in hot water. Then according to your observations prepare a good specimen of the salt by one of the following methods.

(*a*) *Salt soluble in hot water.*

To the hot aqueous solution (or suspension) of the acid in a large basin add the carbonate of the metal whose salt is required until effervescence ceases. Filter from the excess of carbonate, wash the residue with boiling water and evaporate the filtrate until the salt crystallizes. The following salts may thus be obtained:

Lead salts of formic and acetic acids.

Copper salts of formic, acetic and amino-acetic acids.

Zinc salts of lactic and acetic acids.

Calcium and barium salts of formic, acetic, propionic, lactic, benzoic, salicylic, sulphanilic acids, &c.

(*b*) *Salt insoluble or very sparingly soluble in hot water.*

Carefully neutralize the acid with ammonia or dissolve the acid in a slight excess of ammonia and boil off the excess until neutral. Then add a slight excess of a solution of a soluble salt of the metal whose organic salt is required (e.g. $AgNO_3$, $CaCl_2$, $BaCl_2$, $Pb(acet)_2$.) Cool, filter, wash well with water and dry.

N.B.—Calcium citrate, being more soluble in cold water

than in hot water, may be prepared by adding a cold solution of calcium chloride to a cold, neutral solution of ammonium citrate, and then heating to boiling. After a few minutes the salt crystallizes out; filter, wash with hot water and allow to dry.

Isolation of an Organic Acid from its Salts and Esters

Organic acids may be set free from their salts by treatment with a mineral acid, i.e. HCl, H_2SO_4 or HNO_3.

In the case of an ester, the acid is liberated by saponifrcation, i.e. boiling with an aqueous or alcoholic solution of potassium hydroxide. The acid is obtained in the form of its potassium salt:

$$CH_3COOC_2H_5 + KOH = CH_3COOK + C_2H_5OH$$
Ethyl acetate   Potassium
acetate
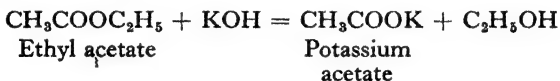
The potassium salt is then treated with a mineral acid.

The treatment of the acid depends, however, on three main factors:

1. The metal present.
2. The solubility of the salt.
3. The solubility of the acid.

Acids may be classified as follows:

A. Acids which are soluble in cold water; mainly **fatty acids,** e.g. formic, acetic, propionic, lactic, oxalic, succinic, malic, malonic, tartaric, citric acids.

B. Acids which are insoluble or very sparingly soluble in cold water; mainly **aromatic acids,** e.g. benzoic, *o*-, *m*-, *p*-hydroxybenzoic acids, *o*-, *m*-, *p*-phthalic acids, cinnammic, sulphanilic, toluic, naphthoic acids, and certain **fatty acids** of high molecular weight.

Identification of the metal.—A small portion of

the salt is ignited in a porcelain or platinum crucible or heated with 50 per cent sulphuric acid to which a little nitric acid has been added. The residue is then dissolved in water or nitric acid, and the solution tested for the metal by the ordinary methods of qualitative analysis. If the residue is insoluble in nitric acid it may indicate the presence of the metals lead, strontium, or barium as the sulphate.

Isolation of the acid.—Treat a small quantity of the salt with one of the mineral acids in order to obtain a soluble salt of the metal. The free acid which is liberated at the same time may behave in one of three ways:

I. It may separate as a crystalline substance or as an oil which ultimately crystallizes.

II. It may separate as an oil which does not crystallize.

III. It may remain in solution.

It is isolated as follows:

I. *Crystalline acid.* (Class B).

(i) Heat the substance in a porcelain crucible; if a residue remains, the substance is an inorganic salt and not an organic acid.

(ii) Heat the remainder of the original substance (if organic) with a mineral acid which forms a soluble salt with the metal. Cool well, filter off the acid, wash and recrystallize the acid from a suitable solvent (test with a small portion at first), dry and take the melting-point. Test for the acid as in Chapter XXIV, p. 555.

II. *Oily acid.* (Class B).

Liberate the free acid from the original substance as already described; cool the solution. The acid is then extracted by treatment with a suitable solvent, such as ether, chloroform, or carbon bisulphide.

Distil off the solvent, add anhydrous calcium chloride to the oily residue and again distil, noting the temperature at which the acid distils.

III. *Soluble acid.* (Class A).

This may be extracted in a few cases by shaking with a suitable solvent, e.g. ether. If, however, the acid is in combination, the basic radicle must if possible be removed by precipitation as in group analysis, followed by filtration and evaporation of the filtrate to crystallization if it is non-volatile.

(i) The metals lead and silver are removed as chlorides by adding HCl.

(ii) The metals Pb, Cu, Bi, Sb, Fe, Zn, Mn, Ni, are removed as sulphides by passing in hydrogen sulphide.

(iii) The metals Ca, Sr, Ba, are removed as sulphates by warming with dilute sulphuric acid and evaporating.

(iv) The metals Na, K, and the basic radicle —NH_4 cannot be removed by precipitation. The acid is therefore precipitated as an insoluble salt of lead, silver, calcium, barium, &c. by adding an excess of the soluble salt of the metal to be used to the *neutral* solution of the organic salt. If the salt reacts acid it is neutralized with ammonia; if it reacts alkaline, it is neutralized with nitric acid.

The precipitated salt is filtered off and washed, and the metal present is precipitated with a suitable reagent, leaving the organic acid in solution.

The acid set free is extracted:

(*a*) by evaporation, in the case of a non-volatile acid;

(*b*) by converting the acid into the lead salt and placing the anhydrous lead salt in a vertical tube whose lower end is drawn out and fitted into a small flask. Hydrogen sulphide is passed over the lead salt, converting it into black lead sulphide, and the free acid runs into the flask and is purified by distillation. This method is used for volatile acids such as formic, acetic, and propionic acids.

Preparation of Salts of Organic Bases

1. Hydrochlorides, Sulphates, Nitrates, &c.

It is usual to prepare the hydrochloride of the base, and in order to obtain a fair specimen of the salt about 15 gm. of the base should be dissolved in hot dilute acid. The solution is filtered hot, and the filtrate allowed to crystallize. When quite cold the precipitated salt is filtered off by means of the filter pump and the crystals are washed with small quantities of cold water. The salt is then removed and the crystals dried, first by pressing them between filter papers and then by allowing them to dry in a warm atmosphere.

(Use Aniline, Ethylamine, Benzylamine, Diethylamine, Triethylamine.)

The hydrochlorides of certain bases, e.g. phenyl pyridines, can be prepared by passing dry hydrogen chloride into a dry ethereal solution of the base.

2. Oxalates.

These can be obtained by mixing equimolecular amounts of hot alcoholic solutions of the base and of oxalic acid and allowing to crystallize until cold.

The oxalate is filtered off, washed with alcohol and dried.

The alcohol residues are collected and recovered by distillation.

(Use Benzylamine, Aniline, Diethylaniline.)

In some cases the acid oxalate is prepared instead of the normal salt.

3. Gold and Platinum Double Salts.

These are obtained by dissolving the base in dilute hydrochloric acid and adding a solution of either auric chloride or platinic chloride and allowing to crystallize. It is usual to prepare the platinum double salt.

These salts have the composition: $R \cdot HAuCl_4$, $R_2H_2PtCl_6$, where R is a molecule of the organic base.

As a rule they are very sparingly soluble in water, but crystallize well. Those which are soluble, e.g. triethylamine platinichloride, can be precipitated in the crystalline state by adding alcohol.

In both cases the double salts are filtered off, washed either with water or alcohol and allowed to dry.

(Use Ethylamine, *p*-xylidene, Benzylamine, Pyridine.)

Isolation of a Base from its Salts

Decomposition of the Salt.

The salt is taken either in solution or in suspension; an excess of alkaline hydroxide is added, and the mixture is gently warmed and then shaken vigorously for some time. The base is thus liberated in one of the following ways:

1. As oily drops, e.g. aniline and its homologues.

2. As crystals or as an oil which crystallizes on standing, e.g. the naphthylamines.

3. In solution, e.g. alkylamines, pyridine.

Extraction of the Base.

The bases so liberated may be recovered by various methods:

(*a*) By distillation in the case of bases which are volatile, such as methyl-, ethyl-, propyl-amines.

(*b*) By extraction with a suitable solvent, usually ether, but sometimes chloroform, carbon disulphide, &c.

The solvent containing the base is allowed to run into a distilling flask containing solid potash or anhydrous potassium carbonate to dry the solution. The solvent is then distilled off from the water bath and the base recovered by

distillation and finally purified either by redistillation or by recrystallization.

(c) By filtration if the base is a solid, followed by recrystallization from a suitable solvent.

Preparation of Organic Salts

The following examples are considered in detail.

$$\text{Ammonium Oxalate,}\quad \begin{matrix} \text{COONH}_4 \\ | \\ \text{COONH}_4 \end{matrix} \cdot H_2O$$

Solubility. At 20° C., 7·05 gm.; at 100° C., 41·34 gm. in 100 c.c. of water.

Procedure.—Weigh out 20 gm. of oxalic acid crystals and dissolve in 200 c.c. of distilled water. Add concentrated (0·880) ammonia from a burette with constant stirring. Continue adding the ammonia until a drop removed on the end of a glass rod and placed on a piece of red litmus paper just changes it to blue. Between 17 and 18 c.c. of ammonia will be required. Boil the solution to expel the excess of ammonia, then add distilled water to replace that which has evaporated. The total volume should be about 240 c.c. Filter whilst hot into a clean beaker; if the filtrate is not clear, reheat and refilter. Allow to crystallize until cold, then pour off the mother liquor as completely as possible. The crystals are then placed on filter paper to dry.

$$\text{Acid Ammonium Oxalate,}\quad \begin{matrix} \text{COOH} \\ | \\ \text{COONH}_4 \end{matrix} \cdot H_2O$$

This is made in precisely the same way as the normal salt, but the oxalic acid solution is divided into two equal parts; one portion is neutralized and the other added to it. Filter hot and allow the salt to crystallize. Or proceed as for the normal salt, but use only half quantities and before filtering add 10 gm. of oxalic acid crystals dissolved in the smallest possible quantity of water.

Urea Oxalate, $[CO(NH_2)_2]_2 \cdot (COOH)_2$

Solubility.   At 15° C., 4·4 gm. in 100 c.c. of water.

Procedure.—To 6 gm. of oxalic acid crystals dissolved in 25 c.c. of boiling water add, while boiling, 5 gm. of urea dissolved in 25 c.c. of water.   Filter off the hot solution immediately and if necessary reboil the filtrate and pass it through the same filter paper.   Repeat until the solution is quite clear.   Allow to crystallize until cold;   separate and dry the crystals as described under ammonium oxalate.

Sodium Acetate, $CH_3COONa \cdot 3H_2O$

Solubility.   At 20° C., 30 gm.; at 50° C., 64 gm. in 100 c.c. of water.

Procedure.—Dilute 45 c.c. of glacial acetic acid by adding 100 c.c. of water.   Add gradually to 40 gm. of anhydrous sodium carbonate in an evaporating basin.   After the first initial reaction has subsided, heat gently until solution is complete.   The solution should be clear, with an acid reaction; if not acid, add a little more acetic acid until it is just faintly acid.   Now evaporate the solution to complete dryness, with constant stirring to prevent spurting.   The basin is then placed on a pipe-clay triangle on a retort stand and the contents strongly heated with constant stirring until fusion takes place.   The fused mass is poured out on to an iron tray, when it solidifies.   The hard cake is powdered up and kept in a dry stoppered bottle.   This sodium acetate can be used for the preparation of ethyl acetate.   Crystals may be obtained from the faintly acid solution in the usual way.

Lead Acetate, $(CH_3COO)_2Pb \cdot 3H_2O$

Solubility.   At 15° C., 46 gm.; at 20° C., 60 gm.; at 100° C. 200 gm. in 100 c.c. of water.

Procedure.—Weigh out 20 gm. of litharge into a porcelain basin. Add 15 c.c. of distilled water and macerate the oxide with a pestle until a paste is obtained. To the pasty mass add 12 c.c. of glacial acetic acid in small quantities at a time, grinding well the whole time. Now add 20 c.c. of distilled water and warm gently to boiling. If the litharge is pure a clear solution should ultimately result, but frequently the lead oxide contains impurities, and small particles of lead and other impurities remain at the bottom of the basin. The solution is then filtered off into a beaker and the filtering continued through the same filter paper until a clear solution is obtained. Cover the beaker with a clock glass and allow to stand as far away from the fume cupboard as possible, since hydrogen sulphide discolours the crystals which separate, owing to the formation of black lead sulphide.

Lead acetate exhibits supersaturation. Hence crystals may not separate on cooling or even when cold. It is therefore advisable to keep the vessel from which this solution has been filtered and add one of the crystals to the supersaturated solution, when immediate crystallization takes place. Remove the mother liquor when cold, and scrape out the crystals on to a porous plate to dry. Complete the drying on filter paper, if possible in a room where there are no hydrogen sulphide fumes.

Lead Formate, $(HCOO)_2Pb$

Solubility. At 15° C., 1·6 gm.; at 100° C., 18·2 gm. in 100 c.c. of water.

Procedure.—Weigh out 9 gm. of litharge into an evaporating basin, add 20 c.c. of a 25 per cent solution of formic acid and grind into a paste with a pestle. Transfer the contents of the basin to a beaker, using 250 c.c. of distilled water to wash out the mixture completely. Boil until the lead oxide dissolves. Filter into a clean beaker; allow to cool until crystallization takes place.

Copper Formate, $(HCOO)_2Cu \cdot 4H_2O$

Solubility.   Not published.

Procedure.—Weigh out 10 gm. of pure cupric oxide into a small beaker, add 50 c.c. of a 25 per cent solution of formic acid, stir with a glass rod and heat until the cupric oxide has dissolved. Add a further 20 c.c. of distilled water, boil and filter while hot. Recrystallize from hot water.

Zinc Lactate, $(CH_3CHOH \cdot COO)_2Zn \cdot 3H_2O$

Solubility.   At 15° C., 1·9 gm.; at 100° C., 16·7 gm. in 100 c.c. of water.

Procedure.—Counterpoise on a pair of scale pans a 250 c.c. beaker and weigh into it 10 gm. of strong lactic acid, followed by 3 gm. of zinc oxide. To this mixture add 50 c.c. of water and mix the contents well with a glass rod. Heat very gently at first, otherwise the beaker may crack. While the mixture is hot add 100 c.c. of water, a little at a time, with constant stirring. Finally boil well until all the zinc oxide has dissolved. Filter and allow to crystallize. Examine the crystals under the microscope.

Additional Preparations

Ethyl Oxalate, $\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array}$
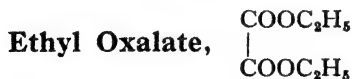
Procedure.—A wide-mouthed round-bottomed flask is fitted with a cork pierced with two holes. Through one hole is inserted an inlet tube reaching almost to the bottom of the flask and to the other a fractionating column connected to a Liebig's condenser. 25 gm. of oxalic acid crystals and 50 c.c. of alcohol are placed in the flask, and the mixture is heated to boiling-point on the water bath. Meanwhile 200 c.c. of alcohol are heated in a separate flask on a water bath. When the first mixture is boiling the alcohol vapour

from the second flask is admitted through the inlet tube. The reaction is as follows:

$$\begin{array}{l} \text{COOH} \\ | \\ \text{COOH} \end{array} \cdot 2H_2O + 2C_2H_5OH = \begin{array}{l} \text{COOC}_2H_5 \\ | \\ \text{COOC}_2H_5 \end{array} + 4H_2O$$

$$\qquad \text{Oxalic acid} \qquad\qquad\qquad \text{Ethyl oxalate}$$
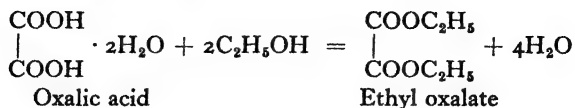
The water liberated during the reaction is then distilled off. When no further distillate of water is obtained the boiling is stopped, the inlet tube is removed and replaced by a thermometer, and the ethyl oxalate in the flask is distilled over, using the fractionating column; the liquid which boils at a temperature over 150° C. is collected. Solid calcium chloride is then added to the distillate to remove the last traces of water and the dehydrated ethyl oxalate is redistilled, the portion boiling at 186° C. being collected (about 25 c.c.)

Bromobenzene, C_6H_5Br

Procedure.—Into a small dry flask measure 50 c.c. of pure dry benzene. Add 0·5 gm. of aluminium-mercury couple (made by adding aluminium foil to a strong solution of mercuric chloride for a minute, then removing the foil and washing it first with water, then with alcohol, and finally with benzene). Attach the flask to a reflux condenser fitted at its upper end with a dropping funnel and also a long exit tube connected at the bottom with a funnel dipping into water contained in a beaker (fig. 54).

Add very slowly to the benzene in the flask 20 c.c. of bromine by means of the dropping funnel; the addition of the bromine should occupy at least half an hour. The bromine reacts with the benzene with considerable evolution of heat, forming bromobenzene and hydrogen bromide:

$$C_6H_6 + Br_2 = C_6H_5Br + HBr$$
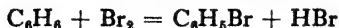
The hydrogen bromide evolved escapes by the exit tube and is absorbed by the water in the beaker.

The flask is allowed to cool, and when cold an excess of dilute potassium hydroxide is added, and the mixture shaken. Now add anhydrous calcium chloride, allow to stand until clear, and pour off the clear solution into a distilling flask. Collect the fraction boiling between 145° and 165° C. Then redistil this fraction in order to collect the portion distilling over between 150 and 160° C.

This is an example of bromination, and of the introduction of a halogen into the benzene nucleus.

Note.—Bromobenzene is a colourless liquid when pure (b. pt. 157° C., sp. gr. 1·502).

Chlorobenzene, C_6H_5Cl

Procedure. — Introduce into a 250 c.c. flask 50 gm. (about 60 c.c.) of pure dry benzene and 0·5 gm. of aluminium-mercury eruple. Weigh the flask and its contents. Attach the flask to a reflux condenser fitted at its upper end with a cork carrying two pieces of glass tubing, one dipping into the benzene through
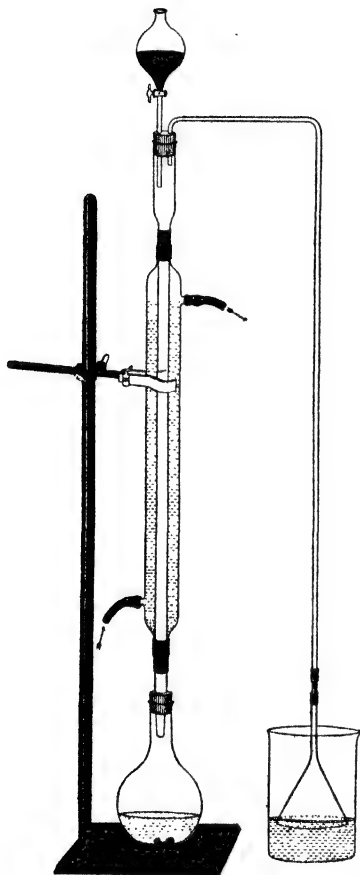
Fig. 54.—Preparation of Bromobenzene

the condenser and the other connected externally as described under bromobenzene. Then pass dry chlorine very slowly into the benzene; heat is generated during the reaction and

the hydrogen chloride evolved is absorbed in the water. The chlorine is allowed to pass until the contents of the flask have gained about 22 gm. in weight, i.e. the theoretical amount calculated from the following equation:

$$C_6H_6 + Cl_2 = C_6H_5Cl + HCl$$
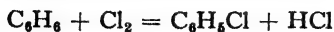
78 gm. benzene $\equiv$ 112·5 gm. chlorobenzene (34·5 gm. increase in weight.)

∴ 50 gm. benzene $\equiv$ 22·1 gm. increase.

The flask is cooled and removed periodically in order to ascertain the increase in weight. When the reaction is complete, the flask is allowed to cool and the contents are poured into 75 c.c. of water contained in a separating funnel. The bottom layer of chlorobenzene is run off, and washed first with sodium hydroxide and then with water. Anhydrous calcium chloride is then added; the liquid is allowed to stand until clear and the clear solution is poured into a distilling flask. The fraction boiling between 128 and 136° C. is collected. Yield about 35 gm.

This is an example of chlorination, and of the introduction of a halogen into the benzene nucleus.

Note.—Chlorobenzene is a heavy colourless liquid, b. pt. 132°, sp. gr. 1·128. It has a pleasant smell.

Nitrobenzene, $C_6H_5NO_2$

Procedure.—Into a 500 c.c. flask measure 60 c.c. of benzene. Into another flask measure 80 c.c. of concentrated sulphuric acid and add gradually 70 c.c. of concentrated nitric acid. Cool this mixture and when cold add it in very small quantities at a time to the benzene. Shake well after each addition and cool the flask under running water so that the temperature is not allowed to rise to 50° C., otherwise dinitrobenzene may be formed.

After the addition of the acid the solution is heated on a water bath at about 55° C. for half an hour, using a vertical air condenser. The mixture is frequently shaken whilst the heating proceeds. The contents are then poured into a separating funnel; the nitrobenzene separates as an oily

layer on the surface. The lower layer is removed, and the nitrobenzene is shaken with dilute sodium carbonate solution in order to neutralize any residual acid. The lower layer (nitrobenzene) is then run off into another separating funnel, washed with water, and run into a flask containing anhydrous calcium chloride and allowed to remain until clear. The clear solution is poured into a distilling flask and fractionally distilled, the portion boiling between 204 and 208° C. being collected.

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$$
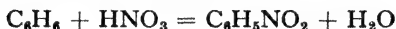
Note.—Nitrobenzene is a yellow oil (m. pt. 5° C., b. pt. 210° C., sp. gr. 1·208) with a smell of bitter almonds.

Meta-dinitrobenzene, $C_6H_4(NO_2)_2(1 : 3)$

Procedure.—Measure 17 c.c. of pure concentrated sulphuric acid into a small dry flask and add to it gradually 20 c.c. of fuming nitric acid of sp. gr. 1·5. Weigh out in a small dry beaker 25 gm. of nitrobenzene made as described above. Add this nitrobenzene 1 to 2 c.c. at a time to the mixture of acids in the flask, shaking well after each addition. When all the nitrobenzene has been added, warm the flask on the water bath for half an hour with constant shaking. Test a portion of the liquid by pouring a drop or two of it into a test tube nearly full of water. If a firm solid product is obtained, the reaction is complete, and the whole of the contents of the flask are poured while still warm into a large volume of water contained in a beaker. The solid which separates is filtered off, washed thoroughly with water, and dried on a porous plate or filter paper.

Take about 5 gm. of the dry product and recrystallize from 25 to 30 c.c. of alcohol. Filter off and dry the purified product on a porous plate. When quite dry take the melting-point (90° C.) and boiling-point of the product (302° C.).

Notes.—1. This is an example of nitration. Note also that the nitro-group already present determines the position to be taken up by the second nitro-group (p. 465).

2. Meta-dinitrobenzene is reduced by alcoholic ammonium sulphide to meta-nitraniline, $C_6H_4 \cdot NH_2 \cdot NO_2$ (1 : 3).

3. Meta-dinitrobenzene and meta-nitraniline are both reduced by tin and hydrochloric acid to meta-phenylene diamine, $C_6H_4(NH_2)_2$ (1 : 3).

Benzene Sulphonic Acid, $C_6H_5SO_2 \cdot OH$

Procedure.—Into a small flask fitted with a reflux condenser measure 60 c.c. of fuming sulphuric acid (or 67 c.c. of concentrated sulphuric acid). Add 35 c.c. of benzene a little at a time with constant shaking. Make sure that the benzene added has completely dissolved before adding a fresh quantity and that the flask is kept cold under the tap.

$$C_6H_6 + H_2SO_4 = C_6H_5SO_2OH + H_2O$$

If concentrated acid is used the flask should be heated for 6 to 8 hours with constant shaking.

The solution now contains benzene sulphonic acid. The free acid is extracted by pouring the contents of the flask into a large quantity of water and adding barium carbonate made into a cream with water, in order to precipitate the excess of sulphuric acid as barium sulphate and to form barium benzene sulphonate, which remains in solution. The solution is filtered hot, and on cooling the filtrate barium benzene sulphonate is deposited.

The benzene sulphonic acid is set free from this salt by adding the calculated amount of sulphuric acid in order to precipitate the barium as sulphate.

$$Ba(C_6H_5SO_2O)_2 + H_2SO_4 = 2C_6H_5SO_2OH + BaSO_4$$

Barium benzene sulphonate	Benzene sulphonic acid
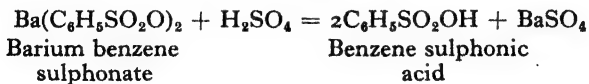
The barium sulphate is filtered off and the filtrate evaporated to a small bulk and allowed to crystallize (m. pt. 65° C.).

Notes.—1. This is an example of sulphonation.

2. The alkali salts of this acid can be obtained by adding the requisite amount of the alkali carbonates either (*a*) to
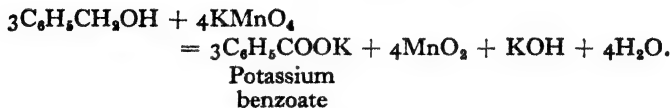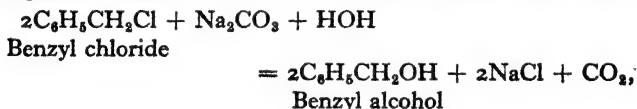
the free acid or (b) to the barium salt. Insoluble barium carbonate is precipitated and filtered off and the filtrate evaporated to crystallization:

$$Ba(C_6H_5SO_2O)_2 + K_2CO_3 = 2C_6H_5SO_2OK + BaCO_3$$

Barium benzene   Potassium benzene
sulphonate   sulphonate
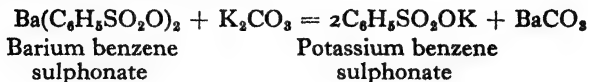
Benzoic Acid, C_6H_5COOH

Procedure.—Weigh out 8·5 gm. of potassium permanganate into 150 c.c. of distilled water contained in a beaker. Warm gently to ensure solution. Into another beaker weigh out 4 gm. of anhydrous sodium carbonate and dissolve in 50 c.c. of water.

Counterpoise a 500 c.c. flask and weigh into it 5 gm. of benzyl chloride. To this add the sodium carbonate solution, together with a few pieces of broken porous pot to prevent bumping. Fit the flask with a reflux condenser and boil gently. The top of the condenser is fitted with a tap funnel, from which the potassium permanganate is slowly dropped; the boiling is continued until the pink colour of the permanganate has disappeared, leaving a brown precipitate of manganese dioxide. This should take two to three hours.

$$2C_6H_5CH_2Cl + Na_2CO_3 + HOH$$

Benzyl chloride

$$= 2C_6H_5CH_2OH + 2NaCl + CO_2,$$

Benzyl alcohol

$$3C_6H_5CH_2OH + 4KMnO_4$$
$$= 3C_6H_5COOK + 4MnO_2 + KOH + 4H_2O.$$

Potassium
benzoate

Sulphur dioxide obtained from a siphon is then passed in until the precipitated manganese dioxide just dissolves. Allow to cool; crystals of benzoic acid separate. These are filtered off and washed with a little cold water.

$$MnO_2 + SO_2 = MnSO_4,$$
$$C_6H_5COOK + SO_2 + HOH = C_6H_5COOH + KHSO_3.$$

Potassium benzoate   Benzoic acid
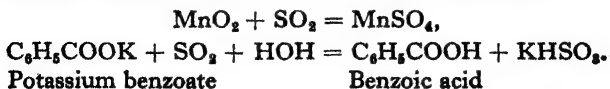
Recrystallize from hot water. The yield is theoretical.

This is an example of the oxidation of a side chain by an alkaline oxidizing agent. Oxidation of a compound containing a substituted side chain is much easier than in one containing an unsubstituted side chain, e.g. toluene.

Note.—When benzoic acid is heated in a dry test tube, it melts and sublimes (m. pt. 121° C.). It distils slowly in steam. For reactions, see p. 547.

Picric Acid, s-Trinitrophenol, $C_6H_2 \cdot OH \cdot (NO_2)_3$.

Procedure.—Counterpoise a porcelain basin and weigh out 12 gm. of phenol into it. Place the basin on a water bath, add 30 c.c. of concentrated sulphuric acid and heat the mixture until a clear solution containing phenol sulphonic acid is obtained.

$$C_6H_5OH + H_2SO_4 = C_6H_4(OH)SO_2OH + H_2O$$
$$\text{Phenol sulphonic acid}$$
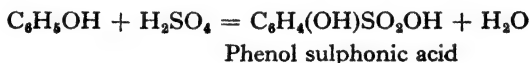
Cool and pour the solution slowly into 50 c.c. of concentrated nitric acid in a flask. The reaction is accompanied by the evolution of a considerable amount of heat; red fumes of oxides of nitrogen are evolved, and the solution becomes deep red in colour. Heat the contents of the flask on the water bath for two hours. Cool and allow to crystallize; a yellow crystalline mass of picric acid separates.

$$C_6H_4(OH)SO_2OH + 3HONO_2$$
$$= C_6H_2(OH)(NO_2)_3 + 2H_2O + H_2SO_4$$
$$\text{Picric acid}$$
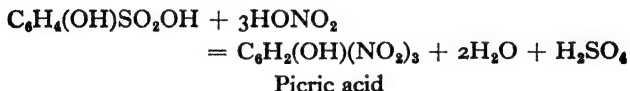
Add water to the yellow mass, shake and filter, using the suction pump; wash well with cold water and recrystallize from hot water; yellow needles separate on cooling. Filter and dry on a porous plate or filter paper. Take the melting-point of the picric acid. Yield 15 gm.

Picric acid is a yellow crystalline substance (m. pt. 122·0° C.). It sublimes on heating. It is used as an explosive and a remedy for burns. It is estimated according to the B.P. by dissolving 2 gm. in hot water and titrating with $N/2$ sodium hydroxide solution, using phenol-phthalein as indicator.

$$1 \text{ c.c. } N/2 \text{ NaOH} \equiv 0·1145 \text{ gm. of } C_6H_3O_7N_3$$
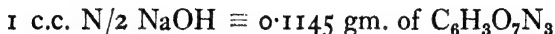
QUESTIONS

1. Add 5 grams of phenylhydrazine to 6·25 gm. of ethyl aceto-acetate in a small flask; shake well. Remove the water from the oily condensation product, and heat the latter on a water bath until a test portion on cooling becomes solid (about 2 hours). Pour the warm product into a little ether; wash the white crystalline product with ether and dry at 100° C. If necessary recrystallise from hot water.

Record the melting-point of your preparation and leave a specimen for inspection. (*II M. B. London.*)

2. Describe briefly with essential experimental details how nitrobenzene may be prepared. State what products may be obtained by the reduction of nitrobenzene, indicating the reducing agents used. (*B.Sc. London, General.*)

CHAPTER XXVII

Estimations

Estimation of Urea by the Urease (Soya-bean) Method

The Soya-bean contains an enzyme, *urease*, which hydrolyses urea completely and at 40° C. rapidly to ammonia and carbon dioxide. The urea is believed to undergo dissociation to ammonia and cyanic acid under the influence of the enzyme. The cyanic acid is then hydrolysed to carbon dioxide and water:

$$CO(NH_2)_2 \rightleftharpoons NH_3 + HNCO$$
$$\text{Cyanic acid}$$
$$HNCO + H_2O = NH_3 + CO_2$$
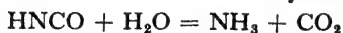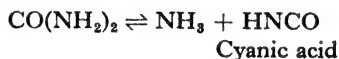
The apparatus is shown in fig. 55.

Two boiling tubes A and B are fitted with corks carrying long straight tubes blown out at the bottom and perforated with a number of fine holes, in order to break up the air into a number of fine bubbles. Each tube is fitted with a splash head C.

In A is placed a mixture of 1 c.c. of urea solution (containing from 1 to 2 gm. of urea in 100 c.c. of water), 0·25 gm. of Soya-bean meal and 3 to 4 c.c. of water. A is then placed in a beaker containing water at 50° C. This beaker is supported so that it can be heated by a Bunsen burner. When the temperature has fallen to 40° C., a small flame is put under the beaker and the temperature kept at 40° C. throughout the experiment.

Tube B is connected to A as illustrated. In B are placed

20 c.c. of N/10 sulphuric acid (or 10 c.c. of N/5) with two drops of methyl red to act as indicator, and the tube is then half filled with distilled water. The splash head of B is connected to a vacuum pump, and air is sucked through at such a rate that any froth which accumulates in A is not drawn over into B. The faster the rate of suction the better, but the suction must be uniform. Air is sucked through
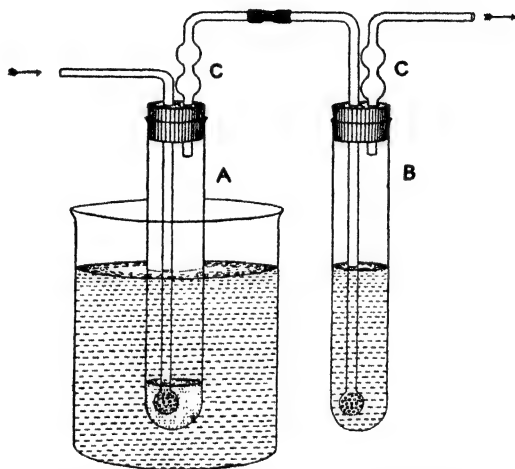

Fig. 55.—Estimation of Urea by the Urease Method

for 30 minutes. The suction is then stopped, and the cork of A raised just enough to allow the introduction of 0·5 gm. anhydrous sodium carbonate powder. The cork is firmly replaced and suction continued for another 30 minutes.

The air tube and splash head of B are rinsed into B, using a wash bottle, and the contents of B titrated with N/10 sodium hydroxide solution. The end point is sharp to a drop.

Results.

Let x c.c. of N/10 NaOH be required for neutralization and let y gm. be the weight of urea taken.

Since $CO(NH_2)_2 \equiv 2NH_3 \equiv H_2SO_4 \equiv 2H$

$$60 \text{ gm. urea} \equiv 2H$$

$$\therefore 30 \text{ gm. urea} \equiv 1H \equiv 1000 \text{ c.c. N solution.}$$

$$\therefore 1 \text{ c.c. } N/10 \ H_2SO_4 \equiv 0\cdot003 \text{ gm. of urea.}$$

Volume of acid used to neutralize the ammonia

$$= (20 - x) \text{ c.c.}$$

Then $(20 - x)$ c.c. $N/10 \ H_2SO_4 \equiv 0\cdot003 \times (20 - x)$ gm. urea in 1 c.c.

$$\equiv 0\cdot003 \times (20 - x) \times 100 \text{ in 100 c.c.}$$

Percentage purity $= \dfrac{0\cdot003 \times (20 - x) \times 100}{y} \times 100.$

Percentage of urea in any given solution, provided 1 c.c. is taken $= 0\cdot003 \times (20 - x) \times 100.$

Example.

Weight of urea taken in 100 c.c.	$= 1\cdot9276$ gm.
Weight of sodium bicarbonate in 250 c.c.	$= 4\cdot2096$ gm.
Factor of $NaHCO_3$	$= \dfrac{4\cdot2096}{21}$ N.
Volume of H_2SO_4 taken in one litre	$= 7$ c.c.

The bicarbonate was used to standardize the acid.

25 c.c. of $NaHCO_3$ neutralized 18·55 c.c. of the H_2SO_4, with methyl orange as indicator.

$$\text{Factor of } H_2SO_4 = \frac{25 \times 4\cdot2096}{18\cdot55 \times 21}.$$

$$= 0\cdot2702 \text{ N.}$$

A decinormal solution was then made by taking 92·75 c.c. of the acid and making up to 250 c.c.

The approximately decinormal solution of sodium hydroxide was next titrated with the standard acid in order to find its factor.

25 c.c. NaOH neutralized 12·95 c.c. H_2SO_4, with methyl red as indicator.

$$\text{Factor of NaOH} = \frac{12\cdot95 \times 0\cdot2702}{25},$$
$$= 0\cdot14 \text{ N.}$$

The excess of acid in B required 9·7 c.c. of 0·14 N NaOH for neutralization.

∴ Amount of N/10 acid used = 20·0 − (9·7 × 1·4) = 6·42 c.c.

but 1 c.c. N/10 H_2SO_4 ≡ 0·003 gm. urea.

∴ 6·42 c.c. ≡ 6·42 × ·003 gm. urea.

$$\text{Percentage purity} = \frac{6\cdot42 \times \cdot003 \times 100}{1\cdot9276} \times 100.$$
$$= 99\cdot9.$$

Notes.—1. It is clear from the above formula that if the percentage of urea in a given solution is over 6, additional acid must be added.

2. If the solution of urea is very dilute, take from 5 to 10 c.c. in A.

3. The sodium carbonate is added in case the solution should contain any acid or acid salt capable of retaining ammonia, as e.g. in urine.

4. This method can be used to determine the percentage of urea in urine if allowance is made for the ammonia present. This can be done by adding the Na_2CO_3 first, sucking over the ammonia, then adding the Soya-bean meal, &c.

5. If the liquid froths badly, as some urines do, a thin layer of a paraffin of high boiling-point is added to A.

6. *Blood urea estimation.* Take 3 c.c. of blood and add 0·25 gm. of Soya-bean meal. Incubate at 40° C. for 20 minutes, then add 5 gm. Na_2CO_3. Take 20 c.c. N/10 acid

in B and 5 c.c. of 0·6 per cent solution of potassium phthalate as a buffer, and back titrate for excess of acid:

1 c.c. N/10 acid ≡ 0·0014 gm. of nitrogen.

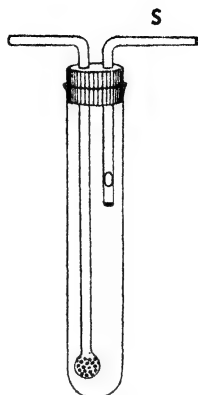7. The splash heads may be replaced by a tube S through which holes are blown at the bottom, as shown in fig. 56.

Estimation of a Sugar

1. **Moisture Content.**—Weigh out accurately about 4 gm. of the sugar in a watch glass. Heat this in a steam oven until the weight is constant. Calculate the percentage loss, which gives the amount of moisture present.

2. **Ash Content.**—Transfer the dried sugar to a weighed platinum crucible. Incinerate portions at a time at as low a temperature as possible. When the sugar is converted into a cake-like mass, stir to accelerate combustion or add a little ammonium nitrate until all black particles disappear; cool and weigh. Calculate the percentage of ash in the usual way.

Fig. 56

3. **Sugar Content:**

I. Volumetric Method.

Prepare Fehling's solution as described on p. 527.

50 c.c. of the mixed solutions (25 c.c. of each) are reduced to cuprous oxide by:

> 0·25 gm. of Glucose.
> 0·25 gm. of Lævulose.
> 0·4035 gm. of Maltose.
> 0·335 gm. of Lactose.
> 0·2375 gm. of Cane Sugar (after inversion).

Standardization of Fehling's solution

Weigh out accurately 5 gm. of pure cane sugar in a CO_2 flask; add 100 c.c. of distilled water and 10 c.c. of pure concentrated hydrochloric acid. Immerse the flask in water at 68° C. for 5 to 10 minutes in order to " invert " the cane sugar, i.e. convert it into glucose. Cool, neutralize the excess of acid with caustic soda (about 100 c.c. $N \cdot NaOH$ or 25 c.c. of bench solution are required), and make up to 500 c.c. with distilled water. Use this sugar solution in the burette.

Take 50 c.c. of the mixed Fehling's solution (25 c.c. of each) in a conical flask and make up to 200 c.c. with water. Heat the Fehling's solution by immersing the flask in boiling water. Keep the solution boiling and add the sugar solution 1 c.c. at a time, allowing half a minute to elapse after each addition of the sugar. Proceed thus until at x c.c. the solution is blue, but at $(x + 1)$ c.c. it is de-colorized. Now repeat the process, running in x c.c. of the sugar as before, always keeping the Fehling's solution boiling. Then add four drops at a time and place the flask upon a white surface in order to judge the colour after the red-brown precipitate of cuprous oxide has been allowed to subside.

The end point can also be ascertained by means of a solution of potassium ferrocyanide solution in dilute acetic acid (one part of ferrocyanide to thirty parts of dilute acetic acid (1 : 6)), placed on a white tile as an external indicator. Any copper still left in solution turns the ferrocyanide brown; if no change in tint is observed all the copper has been precipitated.

The strength of the Fehling's solution is stated in terms of glucose.

Example.—50 c.c. Fehling's solution require 23·75 c.c. of the cane sugar solution.
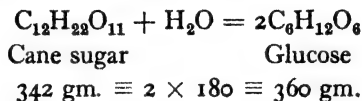
23·75 c.c. of the cane sugar solution contain:

$$\frac{23\cdot75}{500} \times 5 \text{ gm. of cane sugar}$$

$$\equiv \frac{23\cdot75}{500} \times 5 \times \frac{360}{342} \text{ gm. of glucose.}$$

∴ 50 c.c. Fehling's solution ≡ 0·25 gm. glucose.
The ratio 360 : 342 is based on the equation:

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$
Cane sugar   Glucose
342 gm. ≡ 2 × 180 ≡ 360 gm.

Estimation of Glucose.

Weigh out 5 gm. of a sample of glucose, dissolve in distilled water, and make up to 250 c.c. Proceed as for " invert sugar ".

Example.—50 c.c. Fehling's solution require 13·25 c.c. of the glucose solution.
But   50 c.c. Fehling's solution ≡ 0·25 gm. of pure glucose
                                                    (see above)
∴ 13·25 c.c. of glucose solution ≡ 0·25 gm. of pure glucose
∴ 250 c.c. of glucose solution must contain

$$\frac{250}{13\cdot25} \times 0\cdot25 = 4\cdot717 \text{ gm. glucose.}$$

$$\text{Percentage purity} = \frac{4\cdot717}{5\cdot0} \times 100.$$

$$= 94\cdot34.$$

Notes.—1. If the estimation of lactose is undertaken, longer boiling is necessary.

2. With an unknown sugar solution it is necessary to make a preliminary test to judge:

(*a*) whether the solution requires inversion;

(*b*) whether the solution is concentrated or dilute. If concentrated, the solution must be suitably diluted: if dilute, a smaller volume of Fehling's solution must be employed (say 10 c.c.).

II. Gravimetric Method.

The amount of sugar present may be estimated gravimetrically by adding the Fehling's solution in excess to a portion of the sugar solution containing not more than 0·25 gm. of glucose or its equivalent of another sugar, heating the liquid in boiling water for 10 minutes and filtering through an asbestos filter. The cuprous oxide is then estimated by one of the following methods.

1. *Direct weighing.*—In this case the precipitate is filtered through a weighed asbestos filter, washed at once with water, then with alcohol, and finally with ether, dried in a steam oven and weighed.

2. *Reduction* to metallic copper by passing a stream of dry hydrogen or coal gas over the dried cuprous oxide heated in a combustion tube; the copper is allowed to cool in the gas and weighed.

3. *Oxidation* to cupric oxide by passing a stream of air or oxygen over the cuprous oxide heated in a combustion tube. The cuprous oxide is finally weighed when cold.

The following factors are used according to the method employed for glucose, galactose and lævulose:

$$Cu_2O \text{ factor} = 0·5045$$
$$Cu \text{ factor} = 0·5679$$
$$CuO \text{ factor} = 0·4537$$

The weight of substance multiplied by the appropriate factor gives the corresponding weight of glucose.

Example.

Weight of glucose taken   =   0·103 gm.
Weight of filter + Cu_2O = 14·272 gm.
Weight of filter   = 14·08   gm.
Weight of Cu_2O =   0·192 gm.

∴ Actual weight of glucose = 0·192 × 0·5045 = 0·096864 gm.

∴ Percentage purity $= \dfrac{0·096864}{0·103} \times 100 = 94·04$ gm.

Confirmation of result:

Since 0·1985 gm. of Cu_2O is deposited by 0·1 gm. of glucose, 0·192 gm. of Cu_2O is deposited by

$$\frac{0·1}{0·1985} \times 0·192 = 0·09682 \text{ gm.}$$

∴ Percentage purity $= \dfrac{0·09682}{0·103} \times 100 = 94.$

Estimation of Glucose, Lactose, and Cane Sugar by the Polarimeter

The specific rotation of a substance is the number of degrees through which a ray of polarized light of specific wave-length is rotated by a column 1 dm. long of a solution containing 1 gm. of the substance in 1 c.c. of solution. The light most commonly used is that of the D line of sodium. The temperature of the solution at the time of the experiment must be noted. It is assumed here that the temperature is that of the laboratory (20° C.).

The symbol used to denote specific rotation is $\left[\alpha\right]_D^{20}$.

If C denotes the concentration in grammes per 100 c.c.

of solution, A the observed rotation, L the length of the tube in decimetres, we have

$$C = \frac{100A}{\left[a\right]_D^{20} \times L}.$$

The specific rotations of certain sugars are as follows:

	Glucose	Lævulose	Lactose	Maltose	Cane sugar
$\left[a\right]_D^{20}$	52·5°	−92·0°*	52·5°	137°	66·5°

Muta-rotation (p. 374).—Freshly prepared solutions of the first four sugars show specific rotations quite different from those given above, the first three higher, the fourth lower. Such solutions attain the values given:

(*a*) on keeping for 24 hours;

(*b*) on boiling;

(*c*) instantly on being dissolved in one per cent ammonia.

If the rotation of a given solid sugar has to be found, use method (*c*).

Exercises: (*a*) Find the strength of the given solution of glucose.

(*b*) Determine the specific rotation of the given sugar.

An explanation of the polarimeter is given on p. 257 *et seq.*

For exercise B weigh out accurately 5 gm., dissolve and make up to 100 c.c. in the flask provided. Filter the solution till it is absolutely clear. Fill the 2 dm. tube quite full; put on the glass plate; screw on the cap very lightly—it must not press the plate more than is necessary to keep it in position.

See that the handle of the polarimeter is about horizontal; look through the eye-piece and focus it sharply on the middle line of the field; now make the zero of the vernier

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* This diminishes by 0·631° for every degree rise of temperature.

scale coincide with the zero of the scale on the graduated circle by turning the handle slightly. The field should be uniform; if it is not, move the handle till it is, then take the reading. All readings are taken by recording the scale reading nearest to the zero of the vernier; this gives the rotation to the nearest degree below the proper reading, then read the vernier to obtain the decimal place.

When the field is not uniform with the zeros coincident, the reading at uniform field must be added to or subtracted from the final reading, as the case requires. Next place the tube in position and focus sharply as before. If the field is dark on the right, the substance is dextro-rotatory; if dark on the left, it is lævo-rotatory. Do not forget to record this. Suppose the right-hand field is dark; turn the handle clockwise so as to darken the left-hand field to match the right-hand field; when a uniform field has been obtained, take the reading. Repeat at least twice, and take the mean.

Calculate (a) the specific rotation, (b) the concentration of the given solution, using the above formula.

Estimation of Uric Acid, $C_5H_4N_4O_3$

A. Solution of Uric Acid in Water.

A solution of uric acid in water can be titrated with a standard solution of potassium permanganate in presence of sulphuric acid; but the reaction is an empirical one and cannot be represented by an equation. The following numerical relationship must therefore be remembered:

1 c.c. N/20 $KMnO_4$ ≡ 0·00375 gm. of uric acid.

Structurally,
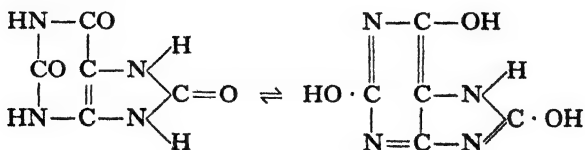
Practice in the observation of the end point is necessary, so the titration is repeated at least once. The conditions described below must always be adhered to. The end point occurs when the permanganate colours the whole liquid pink for the first time and the pink colour persists for two or three seconds. The titration is conducted in a 250 c.c. flask.

Measure out 50 c.c. of the given solution of uric acid: add 50 c.c. of water (the volume to be titrated must always be 100 c.c.). Add 20 c.c. pure concentrated sulphuric acid and titrate at once while hot with N/20 potassium permanganate. Calculate the result in grammes per litre.

A convenient solution is obtained by dissolving 1 gm. (accurately weighed) of uric acid, adding 1 gm. of potassium hydroxide and making up to 1 litre with distilled water. Use 50 c.c. for each estimation.

B. **Uric Acid in Urine** (Folin's modification of Hopkins' Method).

Measure out 200 c.c. of urine (use 100 c.c. pipette) into a flask and add 50 c.c. (by pipette) of a solution made up as follows: 500 gm. of ammonium sulphate; 5 gm. of uranyl acetate; 60 gm. of 10 per cent acetic acid; 650 gm. of water. The uranyl acetate precipitates colloidal matter which makes the filtration slow, and also other substances which reduce permanganate. Shake up and allow to stand fifteen to thirty minutes. Filter through a dry filter paper into a dry vessel. As soon as enough filtrate has been collected, measure out 125 c.c. ($\equiv$ 100 c.c. urine) into a beaker (by 100 c.c. and 25 c.c. pipettes). Add 5 c.c. strong ammonia, stir well, cover with clock glass and leave at least overnight. The crystalline precipitate is ammonium acid urate. Filter through a small filter paper, wash the precipitate on to the paper with 10 per cent solution of ammonium sulphate, and continue washing with the sulphate till the filtrate is

free from chloride. Now wash the precipitate off the filter paper into a 250 c.c. flask (use a wash-bottle with a fine jet). Make up to about 100 c.c., add 20 c.c. pure concentrated sulphuric acid and titrate as before. In order to correct for the slight solubility of the acid ammonium urate, to the uric acid found in 100 c.c. of urine add 0·003 gm. of uric acid. Express the result in grammes of uric acid in 100 c.c. of urine.

Estimation of the Saponification Number of a Fat

The saponification number of a fat is the number of milligrams of potassium hydroxide required to saponify 1 gm. of the fat. This number, known as the " Koettstorfer Number ", is much used in the analytical examination of fats. For example, lard has a K.N. of 195, coconut oil has a K.N. of 246–268. It is clear that the saponification number is merely another method of expressing the average molecular weight of the mixture of fats that constitute the fat under examination.

$$C_3H_5(OOC \cdot R)_3 + 3KOH = C_3H_5(OH)_3 + 3R \cdot COOK$$
$$\text{Fat} \qquad\qquad\qquad \text{Glycerol}$$
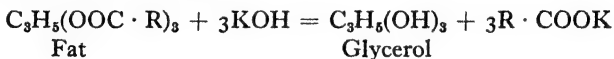
∴ 1 gm. molecule of the fat
$$\equiv 3000 \text{ c.c. N . KOH} \equiv 6000 \text{ c.c. N/2 HCl.}$$

The average molecular weight of the fat is therefore that weight which is equivalent to 6,000 c.c. N/2 HCl.

Solutions required:

1. A solution of alcoholic potash, approximately N/2.

This solution is made by dissolving 30 gm. of pure potassium hydroxide in the least possible quantity of distilled water and making up to a litre with 95 per cent alcohol.

The solution is allowed to stand overnight, and the almost clear solution is decanted off from any impurities which have settled out, into a clean dry bottle.

2. A solution of hydrochloric acid, accurately N/2.

This solution is made by pouring 50 c.c. of concentrated hydrochloric acid into a graduated litre flask and making up to the mark with distilled water. The strength of this solution is found by titrating against a standard solution of sodium hydroxide, using phenol-phthalein as indicator, and adjusting the solution until it is exactly N/2.

In the determination of the saponification number of a fat not more than 2 gm. should be used. To ensure this make a dropping tube about 12 cm. long and of bore 6 to 7 mm., and graduate it with a file, indicating 1 c.c. and 2 c.c. from the drawn-out end, or use a small graduated pipette. Since all fats have a specific gravity of less than 1, if 1 c.c. is delivered from this tube the weight is less than 1 gm.

If the fat is solid, place it in a weighing bottle, then put in the dry dropping tube and weigh. Place the bottle in the oven to melt the fat and then transfer 1·5 to 2·0 c.c. of the fat to a clean dry flask of capacity about 200 c.c. Replace the tube in the weighing bottle and weigh again. This gives the weight of the fat taken. Keep the fat off the neck of the flask.

The flask is then connected to a reflux condenser so that it can be heated on a water bath.

Now add exactly 25 c.c. of the alcoholic potassium hydroxide solution. This must be done very accurately; the number of drops which fall after the bulk of the liquid has run from the pipette are counted. Attach the flask to the condenser, immerse in the water bath, bring to the boil and boil gently for 30 minutes precisely. The flask should be frequently shaken during the heating. While this is going on, the alcoholic potash solution is titrated against the N/2 HCl. This is done by pipetting 25 c.c. of the

alcoholic potash into a flask, adding 10 drops of 1 per cent phenol-phthalein solution, and titrating accurately. Record the figure and find the factor.

After saponification is complete (for any fat that is likely to be given, this is indicated by the liquid being perfectly homogeneous) disconnect the flask and titrate with N/2 HCl, using 10 drops of phenol-phthalein as indicator.

The difference between the two titrations is the number of cubic centimetres of N/2 KOH required to saponify the weight of fat taken for the experiment.

Let W = weight of fat,
       A = number of cubic centimetres of N/2 HCl
              required by the alcoholic potash alone,
       B = number of cubic centimetres of N/2 HCl
              required after saponification:

then

$$K.N. = \frac{(A - B)}{W} \times 28 \cdot 05,$$

since 1 c.c. N/2 KOH ≡ 28·05 mgm. of KOH.

Notes.—1. If the standard KOH is not exactly N/2, the 25 c.c. of alcoholic potash must in the final calculation be multiplied by the factor determined.

2. For accurate determinations of the K.N. a blank experiment should be run simultaneously without the fat, and the number of cubic centimetres of N/2 HCl required to neutralize the 25 c.c. of alcoholic potash, if different, must be substituted for A above.

3. When a fat is rancid and contains free acid the latter must be titrated and allowed for.

4. Used alcoholic solutions should be placed in the alcohol residues bottle.

Example.—To find the saponification number of olive oil.

Weight of flask + olive oil = 37·1316 gm.

Weight of flask = 35·0640 gm.

Weight of olive oil = 2·0676 gm.

25 c.c. of alcoholic potash in
   " blank " experiment required = 20·7 c.c. N/2 HCl (0·973)

25 c.c. of alcoholic potash used
   in saponification required = 5·8 c.c. N/2 HCl

No. of c.c. absorbed by the oil = 14·9 c.c. of factor 0·973

$$\text{K.N.} = \frac{14·9 \times 0·973 \times 0·028 \times 1000}{2·0676}$$

$$= 196.$$

Estimation of the Iodine Value or Number (I.N.) of a Fat

The iodine value of a fat or oil may be defined:

(1) as the percentage of iodine chloride absorbed by a fat or oil, expressed in terms of iodine; or

(2) as the number of grammes of iodine which unite with 100 gm. of fat.

Lard has an I.N. of 46 to 70; human fat, of 59 to 73.

The iodine value depends on the fact that unsaturated fatty acids are capable of forming additive compounds with the halogens, the extent of this combination varying with the degree of unsaturation. In the case of iodine one atom of this element enters at each end of the double bond.

Thus oleic acid, $C_{17}H_{33}COOH$, which has two doubly linked carbon atoms, unites with two atoms of iodine or other halogen:

$$C_{17}H_{33}COOH + I_2 = C_{17}H_{33} \cdot I_2COOH$$
Oleic acid
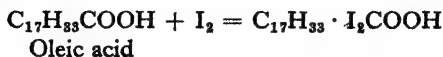
The fatty acids when in combination in a fat or in a substance such as lecithin (a phosphatide), still retain this property; for example, triolein, $C_3H_5(OOC \cdot C_{17}H_{33})_3$, can take up six atoms of iodine.

Direct union of iodine with a fat occurs too slowly for practical purposes. Various methods have been devised to overcome this difficulty.

1. Hübl used an alcoholic solution of iodine and mercuric chloride. This solution acts very slowly and with some fats requires many hours.

2. *Wijs' Method.*—In practice it is found that iodine in conjunction with chlorine is quantitatively absorbed to the fullest extent. Wijs used a solution of iodine monochloride in glacial acetic acid, and found that the I . Cl adds on to the acid as follows:

$$-CH{=}CH- + ICl = -CHI-CHCl-$$
$$\text{e.g.}\quad C_{17}H_{33}COOH + ICl = C_{17}H_{33}I \cdot Cl \cdot COOH$$

Preparation of Wijs' Solution.

Method 1.—Weigh out approximately 13 gm. of iodine into a litre flask. Add glacial acetic acid, shake round until the iodine has dissolved, and make up to the mark with the acetic acid. Titrate 10 c.c. with N/10 sodium thiosulphate solution, using starch solution as indicator.

Then pass in a slow current of dry chlorine until the dark brown colour suddenly changes to orange red. Again titrate 10 c.c. with N/10 sodium thiosulphate. The amount required should be exactly twice the amount originally required; if not, continue to pass the chlorine until the required amount is obtained.

Method 2.—Dissolve a 10 gm. tube of iodine trichloride in 200 c.c. of glacial acetic acid in a large flask. Dissolve separately 12 gm. of iodine in 500 c.c. of glacial acetic acid; add this solution gradually to the trichloride solution until after shaking the colour of iodine is no longer absorbed.

Then add a slight excess of iodine solution. Measure the volume of the solution and add acetic acid until the volume is made up to 1000 c.c. Heat the monochloride solution on the water bath for 15 minutes, then cool. Transfer to a litre flask.

Estimation of the Iodine Value.

For this estimation the quantity of the sample stated below is dissolved in 10 c.c. of carbon tetrachloride, and the solution is placed in a stoppered bottle of capacity about 300 c.c.

Drying or Marine animal oil	0·15 to 0·18 gm.
Semi-drying oil	0·20 to 0·30 gm.
Non-drying oil	0·3 to 0·4 gm.
Solid fat	0·8 to 1·0 gm.

Procedure.—Weigh out the appropriate quantity by means of the dropping tube used for saponification (p. 606) into a dry 300 c.c. stoppered bottle. Keep the fat off the neck of the bottle. Add 10 c.c. of pure carbon tetrachloride or chloroform and shake until the fat is dissolved. Add 25 c.c. of Wijs' solution, shake well, allow to stand in a dark place, for 15 minutes at least with common fats, e.g. butter, lard, olive oil, but up to 1 hour for more unsaturated fats.

In the meanwhile run a blank experiment without the fat. Keep it for the same length of time. Now add 10 c.c. of a solution of potassium iodide (166 gm. of KI per litre) and 100 c.c. of water. Titrate slowly with N/10 sodium thiosulphate solution, shaking well after each addition. When the colour of the solution turns pale yellow add 5 c.c. of starch solution as indicator; continue to add the thiosulphate solution, shaking more vigorously after each addition. The end point is sharp. Note the number of cubic centimetres used.

Now titrate the first bottle in precisely the same way.

The difference between the two readings is the measure of the iodine monochloride added to the weight of the fat

taken, in terms of N/10 sodium thiosulphate; this is taken as equivalent to the same number of c.c. of N/10 iodine.

$$\therefore \text{ 1 c.c. N/10 } Na_2S_2O_3 \equiv 0.0127 \text{ gm. of iodine.}$$

Calculation.

Let A = number of cubic centimetres used in blank titration,

B = number of cubic centimetres used in " fat " titration,

W = weight of fat or oil used.

Then Iodine number $= \dfrac{(A - B) \times 0.0127 \times 100}{W}$.

Example.

Weight of sesame oil taken $= 0.543$ gm.
Titration of blank required $= 45.4$ c.c. of 1.058 N/10 $Na_2S_2O_3$.
Titration of oil required $= 2.5$ c.c. of 1.058 N/10 $Na_2S_2O_3$.
Number of c.c. of iodine used $= 42.9$ c.c.

$$\therefore \text{ Iodine number of sesame oil } = \dfrac{42.9 \times 1.058 \times 0.0127 \times 100}{0.543.}$$

$$= 106.16.$$

For Practice: Use (*a*) castor oil, olive oil, or cod-liver oil; (*b*) coconut oil, lard or tallow.

Soap Analysis

Soaps are evaluated on the basis of (*a*) moisture content; (*b*) fatty acid anhydrides; (*c*) total alkali, subdivided into (i) free alkali, (ii) combined alkali; (*d*) saponification value of the fatty acids; (*e*) iodine value of the fatty acids.

Moisture.—Weigh a clean dry evaporating basin and put into it about 10 gm. of the soap under examination. Cut the soap from the centre portion, not from the exterior.

Weigh again and then place in the steam oven for 3–4 hours. Reweigh and continue the heating until the loss is constant.

Calculate the percentage loss in the usual way.

Fatty acids.—Weigh a CO_2 flask, either stoppered or covered with a watch glass. Then weigh roughly 5 gm. of soap, place it in the flask and weigh again.

Add about 50 c.c. of boiling distilled water; heat very gently with constant shaking until the soap has dissolved.

Run into the flask $N/2$ hydrochloric acid from a burette until the fatty acids liberated rise to the surface, then add 3 drops of methyl orange and continue to add more acid until about 10 c.c. are added in excess. Note the quantity added.

Reheat the flask until the liberated fatty acids melt to a clear liquid. Pour the contents into a separating funnel, care being taken that the larger lumps of fatty acids which may solidify out do not cause splashing on pouring. The separating funnel should contain a little cold water at the bottom.

Rinse the flask out twice with boiling water, each time boiling the water in the flask. Add all washings to the separating funnel. Shake the water round the flask to make sure that no acid remains.

Cool the funnel under the tap; when quite cold, add ether. Wash the CO_2 flask with ether and add the liquid to the contents of the funnel.

Place the stopper in the funnel, shake well, carefully open the tap at intervals to release the pressure of the ether. Allow to stand overnight. The aqueous solution on prolonged standing should be quite clear.

Run out the aqueous solution into a flask. Wash the ether and funnel with water from a wash bottle. Do not shake the funnel, but move the water up and down the sides of the funnel. Add methyl orange, stand for a short time and run off the aqueous layer into the same flask.

Repeat, test again with methyl orange, stand and run off. Remove as much water as possible.

Weigh another CO_2 flask, run in the ethereal solution from the funnel, wash twice, using ether from a wash bottle, collecting the washings in the CO_2 flask. Now connect this flask to a Soxhlet apparatus (fig. 57) or to a condenser and distil off the ether from the water bath. Then disconnect and place in a steam oven for 5 minutes; remove and shake the fatty acids round the sides of the flask in order to hasten the evaporation of any moisture present. Repeat a number of times until the fatty acids are quite clear. Cool in a desiccator; if the liquid is not clear repeat the heating in the oven until it is, then cool and weigh.

Multiply the result by 0·97 to convert to anhydrides.

Total Alkali is estimated by direct titration of 5 gm. of soap with $N/2$ sodium hydroxide solution.

Combined Alkali.—The liberated fatty acids are dissolved in warm alcohol and titrated with $N/2$ alcoholic potassium hydroxide solution, using phenol-phthalein as indicator. Any cloudiness disappears toward the end of the reaction.

Estimation of free NaOH when only Na_2CO_3 is present.

First boil 200 c.c. of distilled water in a litre flask and then dissolve 10 gm. of soap in it, using a bunsen valve to prevent ingress of air. Add a concentrated solution of barium chloride to the soap solution and heat for a time. (The barium chloride solution is made by dissolving 10 gm. of the crystals in 50 c.c. of water.) Cool the solution, filter through a fluted filter paper, rinse out the flask, and pour the washings through the filter.
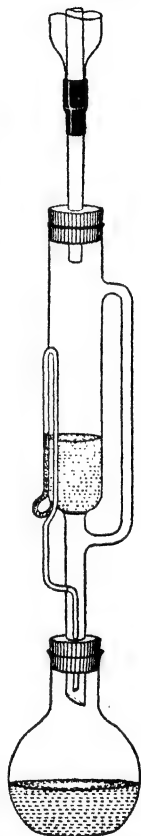

Fig. 57.—Soxhlet Apparatus

Titrate the filtrate and washings with N/10 hydrochloric acid, using phenol-phthalein as indicator.

Example (using, say, Sunlight Soap).

Moisture.

Weight of evaporating basin	$= 57{\cdot}7383$ gm.
Weight of evaporating basin + soap	$= 67{\cdot}6500$,,
Weight of soap	$= \underline{\underline{9{\cdot}9117}}$,,

Weight after heating in oven	$= 65{\cdot}5007$,,
Loss in weight	$= 2{\cdot}1493$,,

$$\text{Percentage of moisture} = \frac{2{\cdot}1493}{9{\cdot}9117} \times 100$$
$$= 21{\cdot}67$$

Fatty acid Anhydrides.

Weight of CO_2 flask + fatty acids	$= 38{\cdot}3786$ gm.
Weight of CO_2 flask	$= 35{\cdot}0626$,,
Weight of fatty acids	$= \underline{\underline{3{\cdot}3160}}$,,
Weight of soap taken	$= 4{\cdot}911$ gm.

$$\therefore \text{Percentage of anhydrides} = \frac{3{\cdot}316 \times 0{\cdot}97 \times 100}{4{\cdot}911}$$
$$= 65{\cdot}5.$$

Combined Alkali.

The above fatty acids required 23·35 c.c. N/2 alcoholic KOH. The factor of the alkali is 1·096.

$$\text{Percentage of } Na_2O \text{ (combined)} = \frac{23{\cdot}35 \times 1{\cdot}096 \times 0{\cdot}0155 \times 100}{4{\cdot}911}$$
$$= 8{\cdot}1$$

Total Alkali.

Weight of CO_2 flask + soap = 54·620 gm.

Weight of CO_2 flask $\quad = \underline{49·315}$,,

Weight of soap $\quad\quad\quad = \underline{\underline{5·305}}$,,

40 c.c. of N/2 HCl (factor 1·124)
were taken $\qquad\qquad\qquad \equiv$ 44·96 c.c. N/2 acid.

15·4 c.c. of N/2 NaOH (factor 1·094)
were required to neutralize excess
of acid $\qquad\qquad\qquad\qquad \equiv \underline{16·85}$ c.c. N/2 acid.

Number of c.c. of N/2 HCl used $\quad = \underline{\underline{28·11}}$

$\therefore$ Percentage of $Na_2O = \dfrac{28·11 \times 0·0155 \times 100}{5·305}$

$\qquad\qquad\qquad = 8·2.$

Titrations with Formaldehyde
(the so-called " Formol " titrations)

I. Ammonia.

Ammonia reacts with formaldehyde to give hexamethylene tetramine; its salts give the same reactions, but the acid is set free and can be titrated. This enables us to estimate the ammonia.

$$4NH_4Cl + 6HCHO = N_4(CH_2)_6 + 6H_2O + 4HCl$$

Procedure.—If a solution of ammonia is given it should, if concentrated, be diluted to about N/10 and exactly neutralized with hydrochloric acid. Do a preliminary titration with 10 c.c., using methyl red and N/5 acid. If the solution is about N/10, proceed with the titration; if not, dilute suitably. Measure out 25 c.c. into a flask, add a few drops of methyl red and titrate with N/5 HCl. This exactly neutralized solution can be used for the aldehyde titration.

Measure out 10 c.c. of formalin; add 4 drops of phenolphthalein and 10 c.c. distilled water; titrate with N/5

NaOH until a distinct pink colour is obtained. Not much NaOH will be required. Add this solution to the neutralized ammonia; the colour will now be pink, owing to the free acid and the methyl red. Titrate this with N/5 NaOH. The pink colour will disappear, and the solution will be yellow; this occurs at about pH 6·5. Continue until the colour is the same distinct pink as the neutralized formaldehyde; that is, about pH 8·5.

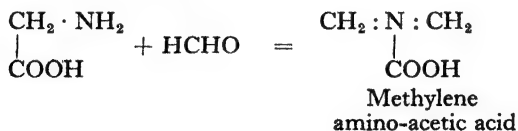Calculate the strength of the ammonia in grammes per litre.

$NaOH \equiv HCl \equiv NH_3$ ∴ 1 c.c. N/5 NaOH ≡ 0·0034 grams NH_3, &c.

Notes.—1. In a urine the phosphates of calcium and magnesium prevent a good end point; some solid neutral potassium oxalate is therefore added. This precipitates the calcium completely, and the magnesium in part. The urine is now neutralized, using phenol-phthalein and N/5 NaOH. Then proceed as above.

2. If the urine contains amino-acids the result is high, because they also react with formaldehyde. In this case the ammonia is better estimated by boiling it off. Then the amino-acids are obtained by difference.

II. Amino-Acids.

Amino-acids, except proline and tyrosine, react with formaldehyde as follows:

$$\begin{matrix} CH_2 \cdot NH_2 \\ | \\ COOH \end{matrix} + HCHO = \begin{matrix} CH_2 : N : CH_2 \\ | \\ COOH \end{matrix}$$
Methylene
amino-acetic acid

The free amino-acid cannot be titrated with any indicator in aqueous solution; but when the basic action of the amino-group is cancelled, as it is on formation of a methylene derivative as above, the acid can be titrated with phenol-phthalein and a strong alkali.

Procedure.—The solution to be titrated should be neutral to phenol-phthalein. If it is not, make it so. For this purpose use 25 c.c. exactly.
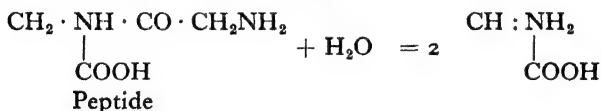
Prepare 10 c.c. of formalin as described above. Add this to the neutralized 25 c.c. Titrate with N/5 NaOH to the same distinct pink as the prepared formalin. If the amino-acid is a known one, express its strength in grammes per litre:

E.g. Amino-acetic acid has molecular weight 75.

∴ 1 c.c. N/5 NaOH ≡ 0·015 gm. amino-acetic acid.

If the acid is not known, express the result in terms of N/10 alkali or as directed.

Notes.—1. The method allows of the determination not merely of a single amino-acid, but also of (*a*) total " amino-acid nitrogen " approximately; (*b*) the progress of hydro-lysis in a liquid which is being hydrolysed by any ordinary method. Suppose the peptide glycylglycine is under examination. One gramme molecule of this would require 1000 c.c. of N · NaOH for the titration; but on complete hydrolysis it would require 2000 c.c. of N · NaOH.

$$\underset{\text{Peptide}}{\overset{\displaystyle CH_2 \cdot NH \cdot CO \cdot CH_2NH_2}{\underset{\displaystyle COOH}{|}}} + H_2O = 2 \quad \overset{\displaystyle CH:NH_2}{\underset{\displaystyle COOH}{|}}$$

(2) Some liquids, particularly after hydrolysis by acid, are so highly coloured that indicators are useless; in such cases devices for removing pigment must be employed. One such is to add a small amount of silver nitrate to the solution and shake it well. The precipitate will often bring down with it by adsorption sufficient pigment to enable an indicator to be used.

(3) Proline gives results which are low, tyrosine results which are high.
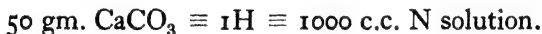
Estimation of the "Hardness" of Water

The hardness of water is represented in degrees. One degree of hardness corresponds to one part of calcium carbonate or its equivalent in 100,000 parts of water. There are two types of hardness of water:

(a) Temporary (removed by boiling).

(b) Permanent (not removed by boiling).

(a) **Temporary hardness** is due to the bicarbonates of calcium and magnesium and is estimated by means of standard acid of one-fiftieth normal strength (N/50). The reaction is represented as follows:

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

$$100 \text{ gm. } CaCO_3 \equiv 2HCl \equiv 2H$$

$$50 \text{ gm. } CaCO_3 \equiv 1H \equiv 1000 \text{ c.c. N solution.}$$

$$\therefore 1 \text{ c.c. } N/50 \text{ HCl} \equiv \frac{0.05}{50} \equiv 0.001 \text{ gm. of } CaCO_3.$$

$$\equiv 1° \text{ Hardness when 100 c.c.}$$
$$\text{water are used.}$$

The N/50 hydrochloric acid is prepared by diluting 20 c.c. of the normal acid up to 1000 c.c. with distilled water.

Procedure.—Take 100 c.c. of the water to be examined, transfer to a conical flask and titrate with N/50 hydrochloric acid, using methyl orange as indicator (this is too strong an indicator to be affected by the liberated CO_2).

Example.—Suppose 15 c.c. of N/50 HCl (factor 0.995)

were required to neutralize the carbonate in 100 c.c. of the sample of water.

1 c.c. N/50 HCl(factor 0·995) $\equiv$ 0·001 $\times$ 0·995 gm. of $CaCO_3$

$\therefore$ 15 c.c. acid $\equiv$ 0·001 $\times$ 0·995 $\times$ 15 gm. of $CaCO_3$

$\therefore$ 100 c.c. of water $\equiv$ 0·001 $\times$ 0·995 $\times$ 15 gm. of $CaCO_3$

                               $\equiv$ 0·014925 gm.

$\therefore$ 100,000 c.c. of water $\equiv$ 1000 $\times$ 0·014925 gm. of $CaCO_3$

                               $\equiv$ 14·925 gm. of $CaCO_3$

Temporary hardness = 14·925°.

(*b*) **Permanent hardness** is due mainly to the sulphates and chlorides of calcium and magnesium, and is estimated by means of N/50 sodium carbonate solution. The reaction is represented as follows:

$$CaSO_4 + Na_2CO_3 = Na_2SO_4 + CaCO_3$$
$$CaCO_3 \equiv Na_2CO_3 \equiv 2H$$
$$50 \text{ gm. } CaCO_3 \equiv 1H \equiv 1000 \text{ c.c. N solution}$$
$$\therefore 1 \text{ c.c. N/50 } Na_2CO_3 \equiv \frac{0·05}{50} \equiv 0·001 \text{ gm. of } CaCO_3.$$

Procedure.—Take 100 c.c. of the sample of water in a porcelain dish. Add a known excess of N/50 sodium carbonate solution to precipitate the calcium and magnesium. Evaporate the solution to dryness on the steam bath. The residue is then taken up with distilled water and the solution filtered, the dish and filter paper being thoroughly washed. The excess of sodium carbonate is "back" titrated with N/50 hydrochloric acid, using methyl orange as indicator.

Notes. — 1. Temporary hardness + Permanant hardness = Total hardness.

2. The magnesium salts present are calculated as calcium carbonate.

3. Although sodium carbonate precipitates calcium carbonate from both the soluble calcium bicarbonate and calcium sulphate, it is only when the chloride and sulphate of calcium are decomposed that the alkali is destroyed, i.e.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$$

Calcium bicarbonate, on the other hand, reacts with the sodium carbonate, causing the passage into solution of an equivalent amount of bicarbonate, as follows:

$$Ca(HCO_3)_2 + Na_2CO_3 = CaCO_3 + 2NaHCO_3.$$
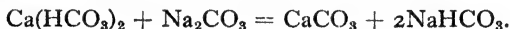
The corresponding magnesium compounds behave similarly.

4. On the English system, hardness is represented as the number of grains of $CaCO_3$ or its equivalent in 1 gallon (70,000 grains) of water, i.e. one degree of hardness corresponds to one part of $CaCO_3$ per 70,000 parts of water.

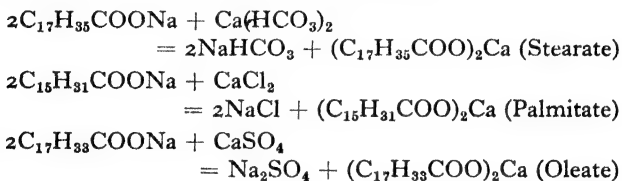## Processes Employed for the Estimation of Hardness

1. **Clark's Method** (1841) is the oldest process and yields inaccurate results if magnesium salts are present in quantity. This process is described below.

2. **Hehner's Method.**—This gives better results, since the presence of magnesium salts does not interfere with the process. A modified description of this method has already been given on p. 619. Instead of N/50 sodium carbonate a mixture of equal volumes of N/50 NaOH and N/50 Na_2CO_3 can be employed. With this solution the calcium salts are precipitated as $CaCO_3$ and the magnesium salts as $Mg(OH)_2$.

3. **The Electrometric Method.**—The chemistry of this method is the same as that described under Hehner's method. For further details the student should refer to standard works on water analysis.

Estimation of Hardness by Soap Solution
(Clark's Method)

This method depends upon the fact that when a solution of soap is added to a solution of a calcium or magnesium salt an insoluble calcium or magnesium soap is produced. The term " hard " was originally applied to the soap-destroying properties of a water. Soap consists of a mixture of the sodium salts of stearic, palmitic, and oleic acids which is soluble in water. These salts react with any soluble calcium salt to form a scum or insoluble soap consisting of a mixture of calcium stearate, palmitate or oleate. The reactions may be represented as follows:

$$2C_{17}H_{35}COONa + Ca(HCO_3)_2$$
$$= 2NaHCO_3 + (C_{17}H_{35}COO)_2Ca \text{ (Stearate)}$$
$$2C_{15}H_{31}COONa + CaCl_2$$
$$= 2NaCl + (C_{15}H_{31}COO)_2Ca \text{ (Palmitate)}$$
$$2C_{17}H_{33}COONa + CaSO_4$$
$$= Na_2SO_4 + (C_{17}H_{33}COO)_2Ca \text{ (Oleate)}$$

The magnesium salts react similarly.

When sufficient soap has been added to react with metallic salts present, the addition of a little more soap produces a permanent lather with the water. In order to estimate the hardness of any water, therefore, it is necessary to prepare standard solutions of soap and of a soluble calcium salt equivalent to a known amount of calcium carbonate.

Standard Solution of Calcium Chloride.

Method I.—Weigh out accurately o·2 gm. of pure Iceland Spar into a porcelain dish and add a little dilute HCl, covering the vessel with a clock glass to prevent loss by spirting. Allow the substance to dissolve and evaporate the solution to dryness on the water bath. Redissolve the residue in distilled water and again evaporate to dryness; repeat these processes once at least to ensure complete

removal of the free hydrochloric acid. Now dissolve the residue in distilled water and make up to 1 litre. This water has a hardness of 20° and 1 c.c. of this solution contains calcium chloride equivalent to 0·0002 gm. of $CaCO_3$.

50 c.c. of this solution, containing an equivalent of 0·01 gm. of $CaCO_3$, are taken for each titration.

Method II.—Weigh out about 5 gm. of anhydrous calcium chloride in a litre flask, dissolve and make up to the mark with distilled water. The strength of this solution is determined by N/10 silver nitrate solution, and an aliquot portion is diluted to 20° of hardness.

$$CaCl_2 \equiv CaCO_3 \equiv 2AgNO_3 \equiv 2H$$

∴ 1 c.c. N/10 $AgNO_3$ ≡ 0·005 gm. $CaCO_3$ ≡ 0·00555 gm. $CaCl_2$.

Example.—4·44 gm. of $CaCl_2$ were dissolved and made up to 1 litre with distilled water. 25 c.c. of this solution required 14·05 c.c. of 0·988 N/10 silver nitrate solution.

Since

1 c.c. of 0·988 N/10 $AgNO_3$ ≡ 0·005 × 0·988 gm. $CaCO_3$,

14·05 c.c. N/10 $AgNO_3$ ≡ 0·005 × 0·988 × 14·05 gm. of $CaCO_3$.

= 0·069407 gm.

Hence 25 c.c. of the calcium chloride solution

≡ 0·069407 gm. of $CaCO_3$.

∴ 100,000 c.c.   „   „   „   „

≡ 277·628 gm. of $CaCO_3$.

Hardness   ≡ 277·628.

In order to obtain a hardness of 20° the original solution should be diluted in the proportion 20 : 277·628, that is, 13·8814 times.

∴ 1 litre should contain 72·04 c.c. of the original solution.

Run into a litre flask 72·04 c.c. of the original solution and make up to the mark with distilled water.

Notes.—1. For very accurate work corrections should be made for the volume occupied by the calcium chloride in the original solution.

2. Method I should be used for accurate work.

Preparation of Soap Solution.

Any of the following three soap solutions can be employed for the estimation of the hardness of water by Clark's Method. For cheapness solution I should be made; for storage purposes either of the other two solutions.

Soap Solution I.—Weigh out 10 gm. of any white soap, such as Primrose, Castile or sodium oleate soap, cut up in fine shavings. Digest with 200 c.c. of clear methylated spirits in a flask, by heating on a water bath until the soap dissolves. Add 300 c.c. more spirit and dilute to one litre with distilled water. Allow to stand overnight and filter.

About 175 c.c. of this solution diluted to 250 c.c. with equal parts of distilled water and spirit will give the required strength.

Soap Solution II.—Weigh 80 gm. of chemically pure oleic acid and dissolve in 300 c.c. of spirit. Add a few drops of phenol-phthalein and run in concentrated alcoholic potash until saponification is complete and a faint purple colour is obtained. Note the volume required and add sufficient alcohol to make 500 c.c. of solution, then dilute to one litre with distilled water. Allow to stand and filter.

Between 60 and 65 c.c. of this solution diluted to one litre with equal parts of spirit and distilled water will give the required strength.

Soap Solution III.—Weigh out 75 gm. of lead plaster (*Plumbi Emplast.* B.P.) and 20 gm. of potassium carbonate in a mortar. Mix intimately and then add alcohol a little at a time, mixing continuously until a creamy mass is

formed. This is stirred with more alcohol, the sediment allowed to subside and the clear solution filtered off through a Buchner funnel. Add a little more alcohol to the sediment and again filter off. Finally transfer the sediment to the funnel with alcohol and wash well with the spirit until 250 c.c. are obtained, then make up to 500 c.c. with distilled water.

About 150 c.c. of this solution diluted to one litre with equal parts of spirit and distilled water will give the required strength.

Titration of Soap Solution.

Place the diluted soap solution of approximate strength in the burette. Measure 50 c.c. of the calcium chloride solution into a stoppered bottle of capacity 250 c.c. Allow 1 c.c. of the soap solution to flow from the burette into the bottle and shake vigorously for a short time. Continue the addition of 1 c.c. of the soap solution at a time, shaking the water well after each addition until a permanent lather remains upon the surface in an unbroken layer for five minutes when the bottle is laid upon its side on the bench.

The approach of the end of the reaction is indicated by (1) the lessening of the sound and shock during shaking, (2) the lather formed becoming more persistent.

Towards the end of the operation the volume of soap solution is reduced until about 0·1 c.c. is added at a time. The soap solution is either diluted with distilled water or strengthened by the addition of more of the original soap solution until 14·25 c.c. are required to produce a permanent lather with 50 c.c. of the standard calcium chloride solution.

Estimation of Total Hardness.

The standard soap solution is now employed to determine the total hardness in various specimens of water, 50 c.c. of such water being used for each titration. If the water

is so hard that more than 16 c.c. of soap solution are required, a suitable measured volume of the water must be diluted to 50 c.c. with boiled and cooled distilled water and again titrated. The number of degrees of hardness is obtained from the number of cubic centimetres of soap solution required by reference to the Hardness Table on p. 640. It will be seen that the hardness is not proportional to the amount of soap solution used; for instance, 0·9 c.c. represents 0° hardness, since this is the quantity required to produce a permanent lather with the 50 c.c. of boiled distilled water used in making up the standard calcium chloride solution.

Notes.—1. If much magnesium salt is present it is best to dilute the water until not more than 7 c.c. of the soap solution are required for titration and to allow the bottle to stand for ten minutes, as the soap solution acts more slowly upon the magnesium salts.

, 2. Carbon dioxide acts chemically upon soap. Hence as a certain amount is present both in the water solution and in the atmosphere it is necessary (*a*) to shake the water vigorously before titration and to suck out the CO_2 after each shaking, and (*b*) to boil and cool the distilled water used for dilution and for making standard solutions.

Estimation of Permanent Hardness.

Measure out 250 c.c. of the water into a flask and weigh. Boil the water gently for half an hour in order to precipitate the salts which cause temporary hardness. Boiled distilled water is added from time to time to replace the water which evaporates. Cool quickly and make up to the original weight with cold, recently boiled, distilled water. Mix well and filter through a dry filter. Titrate 50 c.c. in the usual way and calculate the permanent hardness by reference to the Hardness Table (p. 640).

CHAPTER XXVIII

General Tests for Organic Substances

The following are **liquids:**

Alcohol, Acetone, Formic acid, Acetic acid, Lactic acid.

Aceto-acetic acid is probably a liquid, but it is met with only in aqueous solution as the free acid or, much more probably, as a salt.

Formaldehyde is a gas; it is usually met with in aqueous solution or as its solid polymer Paraformaldehyde.

All the other substances which have to be identified are **solids,** namely:

Oxalic acid, Pentoses, Glucose, Cane sugar, Lactose, Starch, Glycogen, Creatinine, Urea, Uric acid, Cystine, Phenol, Salicylic acid, Tyrosine, Tryptophane, Indole, Indican, Cholesterol.

Smell.—Alcohol, Acetone, Formaldehyde, Formic acid, Acetic acid, Phenol, Indole, all have a characteristic smell. The acids and phenol if given as salts may have no smell. Therefore to test by smell first try the original substance, then acidify with dilute H_2SO_4, heat and smell again.

Solubility.—Insoluble in water: Cholesterol, Cystine, Uric acid. Slightly soluble: Tyrosine.

Note on **Starch.** — Ordinary starch gelatinizes on boiling with water. If a solid is given which shows this behaviour, cool the boiled fluid and test it with a few drops of diluted iodine in KI. A blue colour indicates starch. A soluble starch may be given. This dissolves in hot

water to a clear solution, which gives all the tests for starch.

Cystine and **Tyrosine** are readily soluble in acids and alkalis and are usually met with in solution, especially in alkaline solution.

Glycogen forms a characteristic opalescent solution.

Indican is only likely to be met with in urine.

Reaction.—Most of the substances given are neutral in reaction. The acids may be given as salts, which may have a neutral or even an alkaline reaction. Formaldehyde has an acid reaction, owing to the presence of a trace of formic acid. Phenol, Tyrosine, Cystine are very likely to be given in alkaline solution. Uric acid if given in solution must be treated with alkali until the solution is alkaline.

If the substance is given as a solid, test its solubility in water and in dilute caustic soda. If it is insoluble in both, test for Cholesterol; if it is insoluble in water but soluble in caustic soda, dissolve it in the least possible quantity of caustic soda and proceed as below.

If the substance is soluble in water or is given in aqueous solution, test as follows:
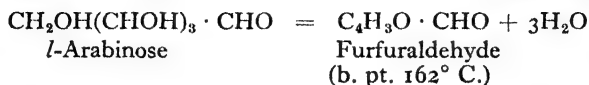
(*a*) Test with litmus.

(*b*) *Molisch's Test.*—To 5 c.c. of solution add a drop of α-naphthol solution, shake up. Pour about 5 c.c. of concentrated H_2SO_4 down side of tube. All **Carbohydrates** give a purple ring.

(*c*) *Fehling's Solution.*—The following reduce Fehling's solution: **Formaldehyde, Glucose, Lactose, Pentoses.**
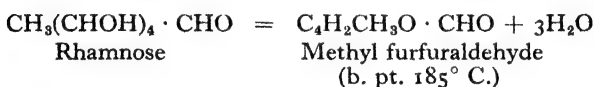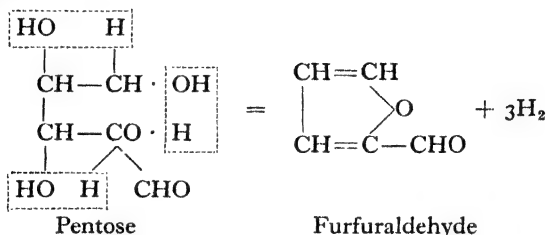
Feeble reduction is given by **Creatinine** and **Uric acid.** The solution is darkened by **Cystine.** If tests (*b*) and (*c*) are both positive, prepare osazone at once. If (*b*) is positive and (*c*) negative, heat some of the solution with a few drops of dilute H_2SO_4 for a few minutes, neutralize the acid, and test with Fehling's solution again. Reduction now indicates **Cane Sugar, Starch, Glycogen.** Taste the original solution.
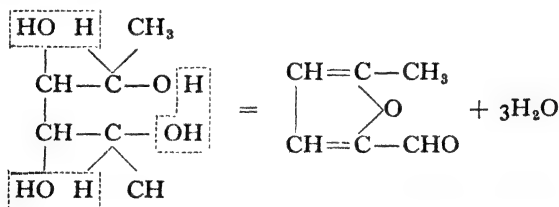
Tests for Pentoses.

1. Boil with HCl (sp. gr. 1·06) in a reflux condenser; pentoses yield furfuraldehyde, whilst certain other carbohydrates, e.g. rhamnose, yield methyl furfuraldehyde:

$$CH_2OH(CHOH)_3 \cdot CHO \;=\; C_4H_3O \cdot CHO + 3H_2O$$

<div style="text-align:center">

l-Arabinose   Furfuraldehyde
(b. pt. 162° C.)

</div>

Structurally,

<div style="text-align:center">

Pentose   Furfuraldehyde

</div>

$$CH_3(CHOH)_4 \cdot CHO \;=\; C_4H_2CH_3O \cdot CHO + 3H_2O$$

<div style="text-align:center">

Rhamnose   Methyl furfuraldehyde
(b. pt. 185° C.)

</div>

Structurally,

The product is then distilled and the distillate tested with aniline acetate paper:

Furfuraldehyde gives a pink colour.

Methyl furfuraldehyde gives an orange colour.

This reaction is used in the quantitative estimation of pentoses.

2. Heat with HCl (sp. gr. 1·19) and a saturated solution of phloroglucinol: a cherry-red colour is observed.

(*d*) If the solution is not neutral, neutralize it by adding a slight excess of ammonia and boiling off the excess. Add $FeCl_3$ solution drop by drop.

Violet or reddish-violet colour: **Phenol, Salicylic acid, Aceto-acetic acid.**

Red colour: **Formic acid, Acetic acid, Creatinine.**

(*e*) *Iodoform Test.*—Given by **Alcohol, Acetone, Aceto-acetic acid, Lactic acid.**

(*f*) *Millon's Test.*—Use a few drops of Millon's Reagent only. Warm. Red colour: **Phenol, Salicylic acid, Tyrosine.**

Millon's Reagent (B.P. method) is made by dissolving 3 c.c. of mercury in 27 c.c. of fuming nitric acid without warming. This solution is then diluted with an equal volume of water. It should be made as required.

(*g*) *Pine Shaving Test.*—A pine shaving moistened with HCl is turned greenish-blue by **Phenol**, cherry-red by **Indole.**

(*h*) *Test for Cystine.*—To 1 c.c. of lead acetate solution add caustic soda till the white precipitate is all redissolved. Add a good deal of the solution. Boil for five minutes. Darkening of the liquid by lead sulphide indicates **Cystine.**

(*i*) *Concentrated H_2SO_4.*—If a solution is given, it must be concentrated. If the solution is acid it must be neutralized before concentrating. Boil in an evaporating basin till strongly concentrated. Cool well. Add H_2SO_4 and heat if necessary.

Formic acid. No charring; evolves CO (test by burning).

Acetic acid. No charring; smell of vinegar.

Oxalic acid. No charring; evolves CO and CO_2 (test for both).

Lactic acid. Chars, evolves CO and acetaldehyde. Repeat in distilling flask and test distillate for aldehyde.

All carbohydrates char readily and strongly on heating.

Cholesterol. Forms red clumps in the cold. Add $CHCl_3$; a green fluorescence in lower layer on standing.

Substances not clearly indicated by any of the above tests are **Creatinine, Tryptophane, Indican, Urea, Uric acid, Formaldehyde.** These must be tested for by their appropriate special tests.

Creatinine.—(1) Forms well-defined crystalline salts with acids. (2) With $KMnO_4$ it is oxidized to methyl guanidine, $(NH_2)C : N \cdot CH_3$. On boiling this compound with HCl, ammonium chloride (test) and methylamine hydrochloride (test) are formed.

Tryptophane: gives *Adamkiewicz's Reaction.*—Add a few drops of glyoxylic acid solution to the substance or to a protein containing tryptophane, and then concentrated sulphuric acid as in testing for nitrates: a violet ring is produced at the junction of the liquids.

Indican.—Hydrolyse with dilute mineral acid and test the hydrolysed liquid for glucose.

Indican in urine is tested for by adding concentrated HCl and a few drops of an oxidizing agent such as hypochlorite solution or ferric chloride, i.e. forming indigo-blue.

Alkaloids *

The alkaloids to be tested for are **Quinine, Morphine, Strychnine** and **Cocaine.**

Alkaloids are organic nitrogenous bases which generally occur in plants in the form of salts of organic acids. Most alkaloids are solid and contain carbon, hydrogen, oxygen, and nitrogen.

If the presence of an alkaloid is suspected in an organic substance, apply the following tests.

Alkaloids give the odour of singed hair when heated.

Dissolve a little of the solid in dilute acetic acid; add a solution of iodine in potassium iodide (*Wagner's Reagent,*

* For Pharmaceutical and Chemists and Druggists Qualifying Examinations

p. 636) or potassio-mercuric iodide (*Mayer's Reagent*, p. 636) or potassio-bismuth iodide (*Dragendorff's Reagent*, p. 636). Alkaloids give a precipitate.

General Tests.

Solutions are alkaline to litmus paper.

1. Evaporate 1 c.c. of the solution to dryness and note odour, &c., on ignition.

2. Try the effect of adding 2 drops of each alkaloid to:

(a) Mayer's reagent.
(b) Wagner's reagent.
(c) Picric acid.
(d) Dragendorff's reagent.

Reagent	Quinine	Morphine	Strychnine
Mayer's	Yellow - white curdy ppt.	Gelatinous pale yellow ppt.	White ppt.
Wagner's	Reddish ppt.	Red-brown ppt.	Brown-yellow ppt.
Picric acid	Yellow ppt.	No ppt.	Yellow ppt.
Dragendorff's	Orange ppt. in dilute mineral acid	Orange-red ppt. in dilute mineral acid	Orange ppt. in dilute mineral acid

3. Heat with soda lime: ammonia is evolved.

4. Try the effect of adding NaOH and NH_4OH: (a) in small quantities, (b) in excess.

Use about 5 drops of each alkaloid solution.

5. Free alkaloids are almost insoluble in water.

Notes.—1. Morphine base is somewhat soluble in water and soluble in excess of NaOH, but not in ammonia, while quinine is soluble in excess of ammonia.

2. Tests with concentrated sulphuric acid (below) must be carried out in dry test tubes.

Quinine, $C_{20}H_{24}N_2O_2$

Quinine is obtained from the bark of *Cinchona Ledgeriana*.

Tests.—1. Moisten a little dry salt with acetic acid and ignite in a dry test tube: coloured fumes condensing to purple drops are obtained.

2. Add a solution of Rochelle salt (potassium sodium tartrate) to a strong solution of the alkaloid: a white precipitate is obtained.

3. To the acetic acid solution add excess of chlorine or bromine water and 2 or 3 drops of ammonia: a green coloration is produced (cf. 6(*a*) below).

Make up a 0·5 per cent solution of quinine sulphate in dilute H_2SO_4.

4. Note fluorescence (light blue, discharged by dilute HCl).

5. Add a small crystal of potassium dichromate to 1 c.c. of concentrated sulphuric acid, shake, and then add 8 to 10 drops of the above quinine solution: a bright green colour is produced.

6. Dilute 5 drops of quinine solution to $\frac{1}{3}$ of a test tube with water, add 2 drops of saturated bromine water and divide into two parts. To

(*a*) add 2 drops of dilute ammonia: a bright green colour is produced. This is known as the *Thalleioquin Reaction*.

(*b*) add 2 drops of potassium ferrocyanide solution and then 2 drops of ammonia: a rose colour is produced.

Morphine, $C_{17}H_{19}NO_3$

Morphine is extracted from Smyrna opium.

Tests.—1. Put a little of the dry salt in a porcelain basin and treat with concentrated nitric acid: a pale orange-red

coloration is produced, not changed by $SnCl_2$ (contrast brucine).

2. Treat a fresh portion with ferric chloride: a blue colour is produced (discharged by mineral acid).

3. Treat with crystalline sodium arsenate and sulphuric acid: a bluish-green colour is produced.

Make up a 0·5 per cent solution of morphine hydrochloride in water.

4. Repeat test 1, taking 1 c.c. of the solution.

5. To 1 c.c. of concentrated H_2SO_4 add 1 drop of formalin and 1 to 2 drops of morphine solution: a rose colour is obtained, turning blue to violet in 10 minutes.

6. To 2 drops add 2 c.c. water and 1 c.c. potassium ferricyanide solution: a green colour is produced.

Then add 1 drop of ferric chloride solution: Prussian blue results.

This test depends on the reducing properties of morphine.

7. Add 1 c.c. to a mixture of 2 drops of potassium iodate solution, 0·5 c.c. of starch solution and 1 to 2 drops of dilute H_2SO_4; just bring to the boil, allow to stand for some time: the blue colour of starch iodide is produced.

This test is very much affected by the conditions of the experiment.

8. To a crystal of potassium dichromate in 1 c.c. of concentrated H_2SO_4 add 5 drops of morphine solution: a green colour or layer is obtained on standing. (Quinine gives a similar reaction.)

9. KOH or NH_4OH gives a white precipitate, soluble in excess of KOH but only sparingly soluble in excess of ammonia.

10. H_2SO_4 and $K_2Cr_2O_7$.—Dissolve solid or solid salt in a few drops of concentrated H_2SO_4, then add a trace of HNO_3 to the cold solution: a deep red colour is produced. Add a small crystal of $K_2Cr_2O_7$: the colour turns to mahogany.

11. *Fröhde's Reagent* (p. 636) gives a purple colour, then green, and finally yellowish-brown.

12. *Mandelin's Reagent* (p. 636) gives a dull purple colour changing to grey.

Strychnine, $C_{21}H_{22}N_2O_2$

Strychnine is extracted from *Strychnos Nux Vomica*.

Make up a 1 per cent solution of strychnine hydrochloride in water.

Tests.—1. Add 2 to 3 drops of the solution to 2 c.c. of concentrated H_2SO_4 and sprinkle in powdered $K_2Cr_2O_7$, PbO_2, or MnO_2: a deep purple colour is obtained, changing to red and finally yellow.

2. HNO_3 dissolves strychnine; on heating, the colourless solution turns yellow.

3. *Mandelin's Reagent* gives a blue colour changing to violet. The addition of ammonia changes the colour to rose red (contrast other alkaloids).

Cocaine, $C_{17}H_{21}NO_4$

Cocaine is extracted from *Erythroxylum Coca* and its varieties.

Tests (to be performed with the solid alkaloid).

1. To 1 c.c. of concentrated H_2SO_4 add a drop or two of rectified spirit and while cold a small quantity of alkaloid. The smell of ethyl benzoate is sometimes noticeable, especially on warming.

Note.—Although this is given as a test, it is not normally possible to detect any smell of ethyl benzoate (omit and mention unreliability of test.).

2. Put a little cocaine in a large watch glass and cover with 1 c.c. of dilute nitric acid; evaporate to dryness on the water bath. To the dry product add 2 drops of concentrated

KOH solution and two drops of alcohol. A smell resembling peppermint is produced; when the smell has disappeared the addition of more alcohol will usually restore it.

Note.—If a solution is given it is necessary to evaporate to dryness and carry out the tests with the solid obtained.

3. Concentrated H_2SO_4 does not colour cocaine, but the subsequent addition of a crystal of $K_2Cr_2O_7$ produces a brown coloration.

4. Concentrated $KMnO_4$ solution gives a purple precipitate of cocaine permanganate.

5. K_2CrO_4 solution added to cocaine solution after a few drops of HCl gives a yellow precipitate.

Brucine, $C_{23}H_{26}N_2O_4$

Brucine is extracted from *Nux Vomica*.

1. Dissolve a little brucine in concentrated H_2SO_4; add a crystal of KNO_3 or a drop of HNO_3. A deep orange colour is developed, which changes to violet on the addition of $SnCl_2$.

The presence of HNO_3 is easily detected by this reaction.

2. Concentrated HNO_3 gives a red coloration; on evaporation the colour changes to yellowish-red and yellow. After all the HNO_3 has evaporated the addition of $SnCl_2$ to the hot solution produces an intense violet colour (contrast morphine).

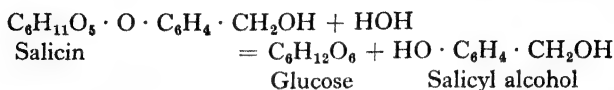3. *Erdmann's reagent* gives a yellow colour changing to red.

4. *Fröhde's reagent* gives a pale-red colour changing to reddish-brown.

5. *Mandelin's reagent* gives a rose colour changing to orange.

Salicin, $C_{13}H_{18}O_7$

Salicin is a glucoside found in the bark of the willow-tree.

Tests.—1. On hydrolysis with acids it yields glucose and salicyl alcohol (saligenin).

$C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH_2OH + HOH$
Salicin $\qquad = C_6H_{12}O_6 + HO \cdot C_6H_4 \cdot CH_2OH$
$\qquad\qquad\qquad$ Glucose $\qquad\quad$ Salicyl alcohol

Test for glucose with Fehling's solution.

2. Add a little concentrated H_2SO_4 to the dry solid: a red coloration is produced.

Reagents for Alkaloids

Mayer's Reagent.—Potassio-mercuric iodide is made as follows:

Dissolve 1·355 gm. of mercuric chloride in 60 ml. of water; dissolve 5 gm. of potassium iodide in 20 ml. of water. Mix the two solutions and add sufficient water to produce 100 ml. (B.P. method).

Wagner's Reagent is a solution of iodine in potassium iodide, approximately N/20.

Dragendorff's Reagent.—Potassio-bismuth iodide is made by adding excess of potassium iodide solution to a solution of bismuth nitrate.

Erdmann's Reagent consists of concentrated sulphuric acid containing 0·5 per cent or less of concentrated nitric acid.

Fröhde's Reagent consists of a solution of about 1 gm. of ammonium or sodium molybdate in 100 c.c. of concentrated sulphuric acid.

Mandelin's Reagent consists of a solution of about 1 gm. of sodium metavanadate or vanadic oxide or another vanadic salt in 100 c.c. of concentrated sulphuric acid.

APPENDIX I

TABLE I

VAPOUR PRESSURES OF WATER FROM 0° C. TO 374° C.

Temp. °C	Pressure in mm. mercury	Temp. °C	Pressure in mm. mercury	Temp. °C	Pressure in mm. mercury
0·0	4·579	7·0	7·514	14·0	11·989
·2	4·7	·2	7·6	·2	12·1
·4	4·7	·4	7·7	·4	12·2
·6	4·8	·6	7·8	·6	12·4
·8	4·9	·8	7·9	·8	12·5
1·0	4·926	8·0	8·046	15·0	12·790
·2	5·0	·2	8·1	·2	12·9
·4	5·1	·4	8·2	·4	13·0
·6	5·2	·6	8·3	·6	13·2
·8	5·2	·8	8·5	·8	13·4
2·0	5·294	9·0	8·610	16·0	13·637
·2	5·4	·2	8·7	·2	13·7
·4	5·5	·4	8·8	·4	13·9
·6	5·5	·6	8·9	·6	14·1
·8	5·6	·8	9·0	·8	14·2
3·0	5·685	10·0	9·210	17·0	14·533
·2	5·8	·2	9·3	·2	14·6
·4	5·8	·4	9·4	·4	14·8
·6	5·9	·6	9·5	·6	15·0
·8	6·0	·8	9·7	·8	15·2
4·0	6·101	11·0	9·845	18·0	15·480
·2	6·2	·2	9·9	·2	15·6
·4	6·3	·4	10·1	·4	15·7
·6	6·4	·6	10·2	·6	15·9
·8	6·4	·8	10·3	·8	16·2
5·0	6·543	12·0	10·519	19·0	16·481
·2	6·6	·2	10·6	·2	16·6
·4	6·7	·4	10·7	·4	16·8
·6	6·8	·6	10·9	·6	17·0
·8	6·9	·8	11·0	·8	17·3
6·0	7·014	13·0	11·233	20·0	17·539
·2	7·1	·2	11·3	·2	17·7
·4	7·2	·4	11·5	·4	17·8
·6	7·3	·6	11·6	·6	18·0
·8	7·4	·8	11·8	·8	18·3

TABLE I —(*Continued*)

Temp. °C	Pressure in mm. mercury	Temp. °C	Pressure in mm. mercury	Temp. °C	Pressure in atmospheres
21·0	18·655	28·0	28·358	100	1·0
·2	18·8	·2	28·6	110	1·41
·4	19·0	·4	29·0	120	1·96
·6	19·2	·6	29·3	130	2·66
·8	19·5	·8	29·6	140	3·57
22·0	19·832	29·0	30·052	150	4·69
·2	20·0	·2	30·3	160	6·10
·4	20·2	·4	30·7	170	7·80
·6	20·5	·6	31·1	180	9·88
·8	20·9	·8	31·5	190	12·37
23·0	21·383	30·0	31·834	200	15·33
·2	21·5	31	33·706	210	18·80
·4	21·7	32	35·674	220	22·86
·6	21·9	33	37·741	230	27·56
·8	22·2	34	39·911	240	32·98
24·0	22·383	35	42·188	250	39·17
·2	22·6	36	43·19	260	46·22
·4	22·9	37	44·58	270	54·19
·6	23·2	38	47·08	280	63·17
·8	23·5	39	49·71	290	73·26
25·0	23·763	40	55·34	300	84·58
·2	24·0	45	71·90	310	97·18
·4	24·3	50	92·54	320	111·20
·6	24·6	55	118·11	330	126·67
·8	24·9	60	149·46	340	143·80
26·0	25·217	65	187·64	350	162·71
·2	25·5	70	233·79	360	183·5
·4	25·8	75	289·32	374	217·0
·6	26·1	80	355·47		
·8	26·4	85	433·79	(Critical	
27·0	26·747	90	526·0	Temper-	
·2	27·0	95	634·0	ature)	
·4	27·3	100·0	760·0		
·6	27·8				
·8	28·1				

TABLE II

VAPOUR PRESSURES OF CONCENTRATED POTASSIUM HYDROXIDE SOLUTIONS AT DIFFERENT TEMPERATURES

Temperature °C	30 grams KOH in 100 grams Water	40 grams KOH in 100 grams Water	49 grams KOH in 100 grams Water
10·0	7·31 mm.	6·50 mm.	5·62 mm.
10·5	7·56	6·72	5·81
11·0	7·82	6·95	6·01
11·5	8·08	7·19	6·21
12·0	8·35	7·43	6·42
12·5	8·63	7·68	6·64
13·0	8·92	7·93	6·86
13·5	9·22	8·19	7·09
14·0	9·52	8·45	7·32
14·5	9·83	8·73	7·56
15·0	10·15	9·02	7·81
15·5	10·47	9·31	8·07
16·0	10·81	9·62	8·33
16·5	11·17	9·94	8·60
17·0	11·54	10·26	8·88
17·5	11·91	10·59	9·17
18·0	12·29	10·93	9·47
18·5	12·69	11·29	9·78
19·0	13·09	11·65	10·09
19·5	13·51	12·02	10·42
20·0	13·93	12·40	10·75
22·0	15·60	13·90	12·10

Table III

HARDNESS TABLE

Parts of $CaCO_3$ per 100,000 parts of Water

c.c. of Soap Solution	Parts of $CaCO_3$	c.c. of Soap Solution	Parts of $CaCO_3$	c.c. of Soap Solution	Parts of $CaCO_3$	c.c. of Soap Solution	Parts of $CaCO_3$
0·7	·00	4·6	5·43	8·5	11·05	12·4	17·06
·8	·16	·7	·57	·6	·20	·5	·22
·9	·32	·8	·71	·7	·35	·6	·38
1·0	·48	·9	·86	·8	·50	·7	·54
·1	·63	5·0	6·00	·9	·65	·8	·70
·2	·79	·1	·14	9·0	·80	·9	·86
·3	·95	·2	·29	·1	·95	13·0	18·02
·4	1·11	·3	·43	·2	12·11	·1	·17
·5	·27	·4	·57	·3	·26	·2	·33
·6	·43	·5	·71	·4	·41	·3	·49
·7	·56	·6	·86	·5	·56	·4	·65
·8	·69	·7	7·00	·6	·71	·5	·81
·9	·82	·8	·14	·7	·86	·6	·97
2·0	·95	·9	·29	·8	13·01	·7	19·13
·1	2·08	6·0	·43	·9	·16	·8	·29
·2	·21	·1	·57	10·0	·31	·9	·44
·3	·34	·2	·71	·1	·46	14·0	·60
·4	·47	·3	·86	·2	·61	·1	·76
·5	·60	·4	8·00	·3	·76	·2	·92
·6	·73	·5	·14	·4	·91	·3	20·08
·7	·86	·6	·29	·5	14·06	·4	·24
·8	·99	·7	·43	·6	·21	·5	·40
·9	3·12	·8	·57	·7	·37	·6	·56
3·0	·25	·9	·71	·8	·52	·7	·71
·1	·38	7·0	·86	·9	·68	·8	·87
·2	·51	·1	9·00	11·0	·84	·9	21·03
·3	·64	·2	·14	·1	15·00	15·0	·19
·4	·77	·3	·29	·2	·16	·1	·35
·5	·90	·4	·43	·3	·32	·2	·51
·6	4·03	·5	·57	·4	·48	·3	·68
·7	·16	·6	·71	·5	·63	·4	·85
·8	·29	·7	·86	·6	·79	·5	22·02
·9	·43	·8	10·00	·7	·95	·6	·18
4·0	·57	·9	·15	·8	16·11	·7	·35
·1	·71	8·0	·30	·9	·27	·8	·52
·2	·86	·1	·45	12·0	·43	·9	·69
·3	5·00	·2	·60	·1	·59	16·0	·86
·4	·14	·3	·75	·2	·75		
·5	·29	·4	·90	·3	·90		

TABLE IV

CALIBRATION OF VOLUMETRIC APPARATUS (W. Schloesser)

This table shows in milligrams how much less than 100 gm. is the weight of water which occupies 1 litre, on the assumption that the co-efficient of cubical expansion for glass is 0·000027 under the following conditions: Volumes to be correct at 15° C. Air temperature, 15° C. Barometer, 760 mm. Normal tension of aqueous vapour.

T° C.	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
5	1341	1340	1339	1338	1338	1338	1338	1338	1338	1338
6	1338	1339	1340	1341	1342	1343	1344	1345	1346	1348
7	1350	1352	1354	1356	1358	1360	1363	1366	1369	1372
8	1376	1380	1384	1388	1392	1396	1400	1404	1408	1412
9	1417	1421	1426	1431	1436	1442	1447	1452	1458	1464
10	1471	1477	1483	1489	1496	1503	1510	1517	1524	1531
11	1539	1547	1555	1563	1571	1579	1587	1595	1603	1611
12	1619	1628	1637	1646	1655	1664	1673	1683	1693	1703
13	1713	1723	1733	1743	1753	1764	1775	1786	1797	1808
14	1819	1830	1841	1853	1865	1877	1889	1901	1913	1925
15	1937	1949	1962	1975	1988	2001	2014	2027	2040	2053
16	2066	2080	2094	2108	2122	2136	2150	2164	2178	2193
17	2208	2223	2238	2253	2268	2283	2298	2313	2328	2344
18	2360	2376	2392	2408	2424	2440	2457	2474	2491	2508
19	2525	2542	2559	2576	2593	2610	2627	2645	2663	2681
20	2699	2717	2735	2753	2771	2789	2807	2826	2845	2864
21	2883	2902	2921	2940	2959	2978	2998	3018	3038	3058
22	3078	3098	3118	3138	3158	3178	3199	3220	3241	3262
23	3283	3304	3325	3346	3367	3388	3410	3432	3454	3476
24	3498	3520	3542	3564	3586	3609	3632	3655	3678	3701
25	3724	3747	3770	3793	3816	3839	3862	3886	3910	3934
26	3958	3982	4006	4030	4054	4078	4102	4127	4152	4177
27	4202	4227	4252	4277	4302	4327	4352	4377	4403	4429
28	4455	4481	4507	4533	4559	4585	4611	4637	4663	4689
29	4716	4743	4770	4797	4824	4851	4878	4905	4932	4959
30	4987	5014	5041	5069	5097	5125	5153	5181	5210	5239

Additional small corrections for air temperature and pressure can be made as follows:

For Temperature.—Subtract 4 × (air temperature − 15) mg.
For Pressure.—To the appropriate figure in the table add
1·4 × (barometer reading − 760) mg.
Example.—Temperature of water in flask = 19·8° C.
Barometer = 770 mm.
Air temperature = 23° C.

Then weight of water required to fill the flask is:

1000 gm. − [2663 − 4(23 − 15) + 1·4(770 − 760)] mg.
= 1000 gm. − (2663 − 32 + 14) mg.
= 1000 gm. − 2645 mg. = 997·355 gm.

TABLE V

EXPANSION OF WATER
(Chappuis)

Centigrade temperature	Volume in ml. of 1 gram of water (volume at 4° C. = 1)	Density (Density at 4° C. = 1)	Centigrade temperature	Volume in ml. of 1 gram of water (volume at 4° C. = 1)	Density (Density at 4° C. = 1)
0	1·00013	0·999868	16	1·00103	0·998970
1	1·00007	0·999927	17	1·00120	0·998803
2	1·00003	0·999968	18	1·00138	0·998624
3	1·00001	0·999992	19	1·00157	0·998435
4	1·00000	1·000000	20	1·00177	0·998234
5	1·00001	0·999992	21	1·00198	0·998023
6	1·00003	0·999968	22	1·00220	0·997802
7	1·00007	0·999930	23	1·00244	0·997570
8	1·00012	0·999876	24	1·00269	0·997329
9	1·00019	0·999809	25	1·00293	0·997077
10	1·00027	0·999728	26	1·00320	0·996816
11	1·00037	0·999633	27	1·00347	0·996545
12	1·00048	0·999525	28	1·00375	0·996259
13	1·00060	0·999404	29	1·00404	0·995976
14	1·00073	0·999271	30	1·00434	0·995678
15	1·00087	0·999127			

TABLE VI

Percentage of Absolute Alcohol (C₂H₅OH) by Weight and by Volume for

A. OVER PROOF SPIRIT

Corresponding to the Specific Gravity of the Liquid taken at
60° F. or 15·6° C. WATER = 1

Specific Gravity	Percentage of Ethyl Alcohol		Over Proof (O.P.) Values	Specific Gravity	Percentage of Ethyl Alcohol		Over Proof (O.P.) Values
	By Weight	By Volume			By Weight	By Volume	
	Absolute alcohol			0·825	89·03	92·55	62·26
0·79359	100·00	100·00	75·35	0·826	88·65	92·26	61·76
0·794	99·87	99·92	75·21	0·827	88·27	91·98	61·26
0·795	99·55	99·72	74·87	0·828	87·88	91·69	60·75
0·796	99.22	99·52	74·52	0·829	87·50	91·40	60·24
0·797	98·90	99·32	74·16	0·830	87·11	91·11	59·73
0·798	98·57	99·12	73·80	0·831	86·73	90·82	59·21
0·799	98·24	98·91	73·44	0·832	86·34	90·52	58·69
0·800	97·91	98·70	73·07	0·833	85·95	90·22	58·16
0·801	97·59	98·49	72·71	0·834	85·56	89·91	57·63
0·802	97·25	98·28	72·33	0·835	85·17	89·61	57·10
0·803	96·91	98·06	71·95	0·836	84·78	89·30	56·56
0·804	96·57	97·84	71·56	0·837	84·39	88·99	56·02
0·805	96·23	97·62	71·17	0·838	83·99	88·68	55·47
0·806	95·89	97·39	70·77	0·839	83·60	88·37	54·92
0·807	95·55	97·16	70·37	0·840	83·20	88·06	54·37
0·808	95·20	96·93	69·96	0·841	82·80	87·74	53·81
0·809	94·85	96·69	69·55	0·842	82·40	87·42	53·25
0·810	94·50	96·45	69·13	0·843	82·00	87·09	52·68
0·811	94·15	96·21	68·71	0·844	81·60	86·77	52·12
0·812	93·80	95·97	68·28	0·845	81·20	86·44	51·55
0·813	93·44	95·72	67·86	0·846	80·79	86·12	50·97
0·814	93·08	95·47	67·41	0·847	80·39	85·80	50·39
0·815	92·72	95·22	66·96	0·848	79·98	85·46	49·80
0·816	92·36	94·97	66·51	0·849	79·58	85·12	49·21
0·817	92·00	94·71	66·06	0·850	79·17	84·78	48·62
0·818	91·63	94·45	65·60	0·851	78·76	84·44	48·03
0·819	91·27	94·19	65·14	0·852	78·35	84·11	47·43
0·820	90·90	93·92	64·67	0·853	77·94	83·77	46·83
0·821	90·53	93·65	64·20	0·854	77·53	83·42	46·23
0·822	90·16	93·38	63·72	0·855	77·12	83·08	45·62
0·823	89·79	93·11	63·24	0·856	76·71	82·73	45·01
0·824	89·41	92·83	62·75				

TABLE VI—(*Continued*)

Specific Gravity	Percentage of Ethyl Alcohol		Over Proof (O.P.) Values	Specific Gravity	Percentage of Ethyl Alcohol		Over Proof (O.P.) Values
	By Weight	By Volume			By Weight	By Volume	
				0·889	62·81	70·35	23·27
0·857	76·30	82·38	44·40	0·890	62·38	69·95	22·56
0·858	75·88	82·03	43·78	0·891	61·95	69·55	21·85
0·859	75·47	81·68	43·16	0·892	61·52	69·14	21·14
0·860	75·05	81·32	42·54	0·893	61·09	68·74	20·42
0·861	74·64	80·97	41·91	0·894	60·66	68·33	19·70
0·862	74·22	80·61	41·28	0·895	60·23	67·92	18·98
0·863	73·81	80·25	40·65	0·896	59·80	67·50	18·26
0·864	73·39	79·89	40·02	0·897	59·37	67·08	17·54
0·865	72·97	79·53	39·38	0·898	58·93	66·67	16·81
0·866	72·55	79·16	38·74	0·899	58·50	66·25	16·07
0·867	72·14	78·80	38·10	0·900	58·06	65·83	15·33
0·868	71·72	78·43	37·46	0·901	57·62	65·41	14·59
0·869	71·30	78·06	36·81	0·902	57·18	64·98	13·84
0·870	70·88	77·69	36·16	0·903	56·75	64·56	13·10
0·871	70·46	77·32	35·50	0·904	56·31	64·13	12·35
0·872	70·04	76·94	34·84	0·905	55·87	63·70	11·59
0·873	69·62	76·57	34·19	0·906	55·42	63·26	10·82
0·874	69·19	76·19	33·53	0·907	54·98	62·83	10·06
0·875	68·77	75·82	32·86	0·908	54·54	62·39	9·29
0·876	68·35	75·44	32·19	0·909	54·10	61·95	8·52
0·877	67·93	75·06	31·53	0·910	53·65	61·51	7·74
0·878	67·51	74·68	30·86	0·911	53·21	61·07	6·97
0·879	67·09	74·30	30·18	0·912	52·77	60·63	6·20
0·880	66·66	73·91	29·50	0·913	52·33	60·19	5·42
0·881	66·24	73·52	28·82	0·914	51·88	59·74	4·63
0·882	65·81	73·13	28·14	0·915	51·43	59·29	3·84
0·883	65·39	72·74	27·46	0·916	50·98	58·83	3·05
0·884	64·96	72·34	26·77	0·917	50·53	58·38	2·24
0·885	64·53	71·95	26·07	0·918	50·08	57·92	1·43
0·886	64·10	71·55	25·37	0·919	49·63	57·46	0·62
0·887	63·67	71·15	24·67	0·91976	49·28	57·10	0·00
0·888	63·24	70·75	23·97		Proof	Spirit	

TABLE VI.—B. UNDER PROOF SPIRIT

Specific Gravity	Percentage of Ethyl Alcohol		Under Proof (U.P.) Values	Specific Gravity	Percentage of Ethyl Alcohol		Under Proof (U.P.) Values
	By Weight	By Volume			By Weight	By Volume	
	Proof	Spirit					
0·91976	49·28	57·10	0·00	0·961	27·73	33·56	41·32
0·920	49·17	56·99	0·20	0·962	27·06	32·79	42·67
0·921	48·71	56·52	1·02	0·963	26·37	31·99	44·07
0·922	48·25	56·05	1·84	0·964	25·68	31·18	45·49
0·923	47·79	55·58	2·67	0·965	24·97	30·34	46·96
0·924	47·33	55·10	3·51	0·966	24·23	29·48	48·47
0·925	46·87	54·62	4·35	0·967	23·48	28·69	50·02
0·926	46·40	54·14	5·20	0·968	22·71	27·69	51·62
0·927	45·94	53·65	6·05	0·969	21·93	26·77	53·23
0·928	45·47	53·16	6·91	0·970	21·14	25·83	54·86
0·929	45·00	52·67	7·77	0·971	20·34	24·85	56·53
0·930	44·53	52·18	8·64	0·972	19·53	23·91	58·23
0·931	44·06	51·68	9·51	0·973	18·72	22·94	59·94
0·932	43·59	51·18	10·39	0·974	17·90	21·96	61·65
0·933	43·11	50·67	11·29	0·975	17·08	20·97	63·39
0·934	42·62	50·15	12·19	0·976	16·25	19·98	65·13
0·935	42·13	49·63	13·11	0·977	15·43	18·99	66·85
0·936	41·64	49·10	14·03	0·978	14·61	18·00	68·58
0·937	41·15	48·57	14·96	0·979	13·80	17·02	70·30
0·938	40·65	48·04	15·90	0·980	12·99	16·04	72·01
0·939	40·15	47·50	16·85	0·981	12·20	15·08	73·68
0·940	39·65	46·95	17·81	0·982	11·42	14·13	75·34
0·941	39·15	46·40	18·77	0·983	10·65	13·20	76·98
0·942	38·64	45·85	19·74	0·984	9·91	12·29	78·56
0·943	38·12	45·28	20·74	0·985	9·18	11·40	80·13
0·944	37·60	44·71	21·74	0·986	8·46	10·51	81·66
0·945	37·07	44·13	22·76	0·987	7·76	9·65	83·15
0·946	36·54	43·54	23·79	0·988	7·08	8·80	84·62
0·947	36·00	42·95	24·83	0·989	6·41	7·98	86·06
0·948	35·46	42·35	25·88	0·990	5·76	7·18	87·47
0·949	34·92	41·74	26·95	0·991	5·13	6·40	88·84
0·950	34·37	41·13	28·02	0·992	4·51	5·63	90·18
0·951	33·81	40·50	29·13	0·993	3·90	4·88	91·49
0·952	33·25	39·87	30·24	0·994	3·31	4·14	92·76
0·953	32·67	39·22	31·38	0·995	2·73	3·42	94·02
0·954	32·09	38·57	32·52	0·996	2·17	2·71	95·27
0·955	31·50	37·89	33·71	0·997	1·61	2·02	96·48
0·956	30·90	37·20	34·91	0·998	1·07	1·34	97·67
0·957	30·28	36·50	36·15	0·999	0·53	0·66	98·84
0·958	29·66	35·79	37·40	1·000	0·00	0·00	100·0
0·959	29·03	35·06	38·68				
0·960	28·39	34·33	39·97		Water		

TABLE VII

ATOMIC WEIGHTS, 1937
[International Union of Chemistry, 1937]

	Symbol	At. No.	At. Wt.		Symbol	At. No.	At. Wt.
Aluminium	Al	13	26·97	Neodymium	Nd	60	144·27
Antimony	Sb	51	121·76	Neon	Ne	10	20·183
Argon	A	18	39·944	Nickel	Ni	28	58·69
Arsenic	As	33	74·91	Niobium	Nb		
Barium	Ba	56	137·36	(Columbium)	(Cb)	41	92·91
Beryllium	Be	4	9·02	Nitrogen	N	7	14·008
Bismuth	Bi	83	209·00	Osmium	Os	76	191·5
Boron	B	5	10·82	Oxygen	O	8	16·000
Bromine	Br	35	79·916	Palladium	Pd	46	106·7
Cadmium	Cd	48	112·41	Phosphorus	P	15	31·02
Cæsium	Cs	55	132·91	Platinum	Pt	78	195·23
Calcium	Ca	20	40·08	Potassium	K	19	39·096
Carbon	C	6	12·01	Praseodymium	Pr	59	140·92
Cerium	Ce	58	140·13	Radium	Ra	88	225·97
Chlorine	Cl	17	35·457	Radon	Rn	86	222
Chromium	Cr	24	52·01	Rhenium	Re	75	186·31
Cobalt	Co	27	58·94	Rhodium	Rh	45	102·91
Copper	Cu	29	63·57	Rubidium	Rb	37	85·48
Dysprosium	Dy	66	162·46	Ruthenium	Ru	44	101·7
Erbium	Er	68	167·64	Samarium	Sm	62	150·43
Europium	Eu	63	152·0	Scandium	Sc	21	45·10
Fluorine	F	9	19·00	Selenium	Se	34	78·96
Gadolinium	Gd	64	156·9	Silicon	Si	14	28·06
Gallium	Ga	31	69·72	Silver	Ag	47	107·880
Germanium	Ge	32	72·60	Sodium	Na	11	22·997
Gold	Au	79	197·2	Strontium	Sr	38	87·63
Hafnium	Hf	72	178·6	Sulphur	S	16	32·06
Helium	He	2	4·002	Tantalum	Ta	73	181·4
Holmium	Ho	67	163·5	Tellurium	Te	52	127·61
Hydrogen	H	1	1·0078	Terbium	Tb	65	159·2
Indium	In	49	114·76	Thallium	Tl	81	204·39
Iodine	I	53	126·92	Thorium	Th	90	232·12
Iridium	Ir	77	193·1	Thulium	Tm	69	169·4
Iron	Fe	26	55·84	Tin	Sn	50	118·70
Krypton	Kr	36	83·7	Titanium	Ti	22	47·90
Lanthanum	La	57	138·92	Tungsten	W	74	184·0
Lead	Pb	82	207·21	Uranium	U	92	238·07
Lithium	Li	3	6·940	Vanadium	V	23	50·95
Lutecium	Lu	71	175·0	Xenon	Xe	54	131·3
Magnesium	Mg	12	24·32	Ytterbium	Yb	70	173·04
Manganese	Mn	25	54·93	Yttrium	Y	39	88·92
Mercury	Hg	80	200·61	Zinc	Zn	30	65·38
Molybdenum	Mo	42	96·0	Zirconium	Zr	40	91·22

Note.—In chemical estimations the student should use atomic weights which approximate to the nearer half or whole number, unless instructed otherwise.

The Svedberg Ultracentrifuge

The determination of the molecular weights by Svedberg's ultracentrifuge was mentioned in Chapter I, p. 46, and in view of its extended use in medical and in bacteriological laboratories a brief description of this machine may be of interest.

The earlier centrifuges designed by Prof. T. Svedberg of Upsala from 1924 onwards have undergone many changes. At the present time, the part known as the rotor is somewhat elliptical in shape, grooved at the top and bottom and with a thin knife-like blade at each side (fig. 58). The shape adopted was found to resist the stresses and strains produced at the very high velocity of 65,000 r.p.m. and more; at this velocity the inward pull at the cell is 300,000 times that of gravity, and by this means particles in many stable colloidal solutions are gradually deposited (sedimentation).

The rotor is made of chrome-nickel steel and consists of two halves, each with a plane surface. When these two surfaces are clamped together the chamber becomes vacuum-tight and is then evacuated, as the frictional coefficient of air is high and would lead to overheating. Hydrogen whose frictional resistance is low, is then admitted to produce a pressure of 20 mm. inside, but no more. The rotor is pierced by two holes, one for the test cell and the other for the balancing cell.

The ebonite cell used for the experimental fluid is 18 mm. deep and is surrounded by a thick cylindrical shell of duralumin. This inner cell is compressed between end plates of optically polished crystalline quartz, so that the colloidal or other solution which it contains is clearly visible; only 0·2 ml. of the solution to be tested is required. The cell is then inserted in the rotor together with the compensating cell. To give an idea of the

size of the rotor, it may be marked that the diameter across the cell holes is about eleven inches. Smaller ultracentrifuges are, however, made for laboratory use.

The rotor is then set in motion by means of high-pressure oil which is directed on to small turbines fixed on either end of the main shaft. This turbine oil is supercooled by means of a refrigerating plant, so that the slip bearings are kept at more or less constant temperature. The fluid in the cell is illuminated
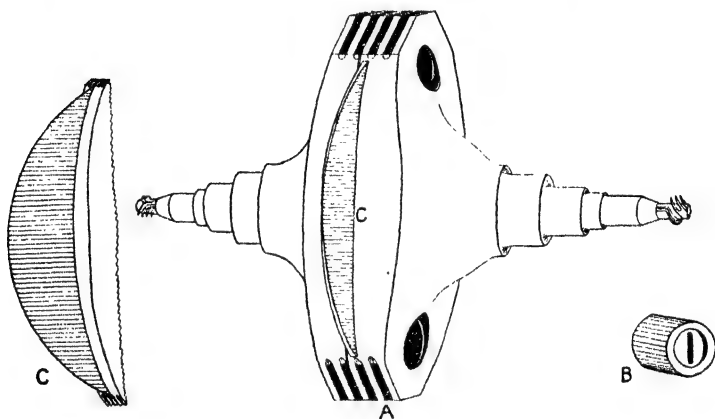
Fig. 58.—The Svedberg Ultracentrifuge
B, The Test Cell. C, The Blade (side view)

by the light from a mercury arc and the changes observed in the fluid are recorded by means of a camera suspended horizontally from the ceiling.

On account of the high frequency with which the pictures are received, the cell appears stationary, and the photographs obtained are quite clear.

This apparatus is used:

1. To determine the molecular weights of colloids and crystalloids, by observing the rate of sedimentation.

2. To separate the constituents of a mixture.

3. To investigate proteins, polysaccharides, dyes, colloids, complex inorganic salts, &c.

4. To measure the sizes of molecules, e.g. of the protein hæmoglobin in the blood; of larger proteins, inorganic salts, &c.

5. To investigate diseases. In cases of scarlet fever, diphtheria, &c., larger proteins, such as globulin, are present in the blood and in cases of pneumonia new proteins have been found. The rate of sedimentation is directly proportional to the size of the particle, so that the larger proteins are deposited first.

6. To measure the sizes of bacteria and viruses.

First Aid in the Laboratory

First Aid Cabinet should contain the following solutions and material.

Bandages.	Clinical thermometer.
Boracic lint, about ½ yard.	Tourniquet.
Absorbent cotton wool, ¼ lb.	Boric acid powder, 1 oz. (for
Oiled silk, ½ yard.	eye lotion).
Triangular bandages.	Sal volatile, 1 oz.
Roller bandages.	Alcohol
Finger bandages.	Permanganate of potash crystals.
Court plaster.	Boracic vaseline, 1 oz.
Eye bath.	Tincture of iodine.
Eye shade.	Phenol (3 per cent solution).
Camel-hair brush.	Friar's balsam, 1 oz.
Clean scissors.	Tin of mustard.
Needles.	Tannic acid (5 per cent solution).
Thread.	Carron oil (lime water and olive
Sterilized gauze.	or linseed oil—equal parts).

In serious accident cases, after the application of first aid the patient should be taken immediately either to a doctor or to a hospital.

FIRST AID TREATMENT

Cuts.—Stop bleeding by placing finger or thumb on bleeding spot.

If small, treat with cotton wool wetted with tincture of iodine or Friar's balsam; see that no fibres remain in the cut, then apply a piece of sterile bandage or adhesive plaster.

If deep, pour in some hydrogen peroxide or apply cotton gauze soaked in aluminium acetate solution, so as to coagulate the blood, then apply a firm pad of antiseptic dressing.

Healing is accelerated by the application of " T.C.P. Ointment ". (T.C.P. is trichlorphenolmethyliodosalicyl).

T.C.P. solution can also be used as a styptic.

Affix a tourniquet if an artery is cut.

Eye.

Reagents.—Wash freely with a large volume of water.

Alkaline chemicals.—Wash with a half-saturated solution of boric acid, using a wash-bottle, then wash eye with a large volume of water.

Acid chemicals.—Wash with a saturated solution of borax, using a wash-bottle, then wash with a large volume of water.

Notes.—1. An eye cup should be used, filled with the appropriate neutralizing liquid, and the eyelids moved in the solution.

2. On no account may either ammonium or sodium bicarbonate solution be used to wash the eye. These are dangerous to the membrane.

Foreign body.—Wash freely with warm water; dip face in a basin of water, opening and closing the eye under water. Remove foreign body with a piece of lint; do not rub foreign body over the eye. After removal of body, one drop of castor oil is dropped into the eye.

Burns.

Do not use water; wash with a 5 per cent solution of tannic acid or apply " Tannafax " jelly or " acriflavine emulsion ". " Tannafax " is a tannic acid jelly containing 0·5 per cent of carbolic acid; this forms a protective covering which peels off when a new skin has been formed.

Carron oil or a 1 per cent solution of phenol in olive oil or a 0·5 per cent aqueous solution of picric acid can also be used.

Chemicals on Skin.

Acids.—Wash freely with much water, then wash with a solution of bicarbonate of soda or of borax.

Apply " Tannafax " for a severe burn.

Alkalis.—Wash freely with much water and then with the boric acid solution or a 1 per cent acetic acid solution. Apply zinc oxide ointment.

Bromine.—Wash freely with much water, then rub glycerine into the skin, which reacts with the bromine which may have penetrated into the skin.

Alternately, after washing treat with a dilute solution of sodium bicarbonate, and then wash with alcohol.

Phosphorus.—Treat by one of the following methods:

(a) Wash with aqueous 5 per cent solution of copper sulphate.

(b) Add a 5 per cent solution of silver nitrate.

(c) Wash with light petroleum. (Be careful, as this liquid is highly inflammable.) Then cover the injury with lint to exclude air.

Chemicals in Mouth.

In every case wash out with large quantity of water several times.

Acids.—Wash mouth out with a solution of lime water or of borax.

Alkalis.—Wash mouth out with a dilute solution of acetic acid. In either case finally wash mouth out with glycerine and thymol.

Poisoning.

Gases.—Remove patient to open air or near an open window. Saturate some lint with ethyl alcohol or sal volatile, apply to nostrils and make patient inhale vapours. In case of hydrogen sulphide, make patient inhale diluted chlorine.

Acids.—Give chalk or magnesia in water.

Alkalis.—Give lemon juice or vinegar or dilute acetic acid.

Carbolic acid.—Give a dose of Epsom salts in water.

Other poisons.—Give mustard in water, white of egg, linseed tea, or other demulcents.

In all cases of doubtful or ineffective treatment of the patient summon a doctor at once.

PREVENTION OF ACCIDENTS

Burning.

Chemicals.—Extinguish burners and remove all inflammable material. Use a fire extinguisher or carbon tetrachloride, not water.

Burning clothing.—Do not use water; wrap a fireproof blanket, rug, coat, or jacket round the patient and roll him on the floor.

Chemicals on Clothes.

Acids.—Wash with ammonia or ammonium carbonate solution.

Alkalis.—Wash with dilute acetic acid, then with water and finally with ammonium carbonate solution.

Chemicals on Benches, &c.

Acids.—Add solid sodium bicarbonate, lime or chalk.

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANSWERS TO NUMERICAL QUESTIONS

For reasons of space full structural formulæ have
not been given

CHAPTER I

P. 3. **1.** C_4H_8O (C_3H_7CHO, butyraldehyde). **2.** C_3H_3NO.

P. 13. **2.** 67·84. **3.** 341·99. **4.** 86·885.

P. 16. **2.** 172·72.

P. 46. **1.** Acetamide, CH_3CONH_2. **2.** C_8H_7S.

3. CH_4O, possibly CH_3OH, methyl alcohol; vapour density required.

4. C_3H_9N (($CH_3)_3N$, trimethylamine).

5. 125·62. **6.** 59·93.

7. $C_6H_{10}O_4$, probably $\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix}$, diethyl oxalate,

or $\begin{matrix} CH_2COOCH_3 \\ | \\ CH_2COOCH_3 \end{matrix}$, dimethyl succinate.

8. C_3H_6O (($CH_3)_2O$, acetone, or C_2H_5CHO, propionaldehyde).

9. 342.

10. C_2H_6O (C_2H_5OH, ethyl alcohol, or ($CH_3)_2O$, dimethyl ether).

11. Empirical formula C_3H_6O; molecular formula C_3H_6O (acetone or propionaldehyde).

12. CH_2I_2 (methylene iodide).

13. $C_4H_8O_4$ ($CH_3(CHOH)_2 COOH$ or $CH_2OH (CHOH)_2CHO$).

15. C_2H_4O (CH_3CHO, acetaldehyde).

17. 0·035 gm. in 100 gm. benzene.

18. 983·41 cm.

19. Compound is an electrolyte and is ionized in solution. Freezing-point −32·77° C.

20. 228. **21.** 65·46. **22.** 119·64. **23.** 153·38.

24. 23·92 atm.

CHAPTER II

4. 25 c.c.

22. C_4H_8 (probably $CH_3CH{=}CHCH_3$, butylene).

CHAPTER III

10. $C_2H_4Br_2$ ($CH_2Br . CH_2Br$, ethylene bromide, or CH_3CHBr_2, ethylidene bromide).

CHAPTER IV

18. $C_4H_{10}O$ (($C_2H_5)_2O$, ether, or C_4H_9OH, butyl alcohol).

CHAPTER IX

11. $-2{\cdot}02°$ C.; discrepancy due to slight ionization.

CHAPTER XI

1. Volume 9·607 litres; 5·49 litres carbon dioxide, 2·745 litres water (as steam), 1·372 litres oxygen.

CHAPTER XVII

2. Molecular formula C_8H_8O ($C_6H_5COCH_3$, acetophenone, or $C_6H_4CH_3CHO$, tolualdehyde).

CHAPTER XXI

1. Empirical formula CH_2O (HCHO, formaldehyde; CH_3COOH, acetic acid).

2. C_2H_6.   **3.** 1·97%.

4. (A) C_7H_5N or C_6H_5CN, benzonitrile;
(B) C_6H_5 COOH, benzoic acid;
(C) C_6H_6, benzene.

6. CH_4N_2O (probably $CO(NH_2)_2$, urea).

7. Molecular formula $C_2H_5NO_2$; structurally,

$$
\begin{array}{ccc}
\mathrm{H} & \mathrm{H} & \mathrm{O} \\
| & | & \| \\
\mathrm{H-\!C-\!C-\!N}{=}\mathrm{O}, & & \text{nitro-ethane.} \\
| & | & \\
\mathrm{H} & \mathrm{H} &
\end{array}
$$
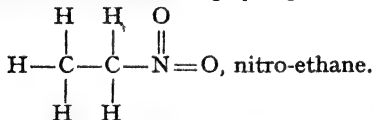
9. (*a*) C_2H_5NO, acetamide; (*b*) CH_3COOH, acetic acid;
(*c*) CH_3CN, methyl cyanide; (*d*) CH_3NH_2, methylamine.

11. CH_6ClN ($CH_3NH_2 . HCl$, methylamine hydrochloride).

12. Hydrocarbon C_7H_8 ($C_6H_5CH_3$, toluene).   Acid $C_7H_6O_2$ (C_6H_5COOH, benzoic acid).

13. Empirical formula C_7H_5; possible molecular formula $C_{14}H_{10}$ (anthracene).

14. $C_4H_{10}O$; commonest compound ($C_2H_5)_2O$, ether, mol. wt. 74.

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